## PART I

# NATURAL POLYMER BLENDS
# AND COMPOSITES

# Starch–Cellulose Blends

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## 2.1 INTRODUCTION

The first polymers used were natural products, especially cotton, starch, proteins, and wool. Early in the twentieth century, synthetic polymers began to be produced. The first polymers of importance, Bakelite and Nylon, showed the tremendous possibilities of the new materials (Sperling, 2006). Global consumption of biodegradable

polymers increased from 14 million kg in 1996 to 68 million kg in 2001 (URL1). The advantages of natural polymers include the renewable resources from which they originate, their biodegradability, and the environmentally friendly products of degradation that are produced (Yu et al., 2007).

Ecological concerns have resulted in a renewed interest in natural and compostable materials and issues such as biodegradability and environmental safety are becoming correspondingly important. Tailoring of new products within a perspective of sustainable development or eco-design is a philosophy that is being applied to more and more materials. This is why components such as natural fibers, and biodegradable polymers are considered as "interesting"—environmentally safe—alternatives for the development of new biodegradable composites (Avérous and Boquillon, 2004).

Among the many kinds of candidates for biodegradable polymer (see Table 2-1), starch is one of the most promising materials for biodegradable plastics because it is a

**TABLE 2-1   Overview of Natural Biodegradable Polymers (Biopolymers)**[a]

| | |
|---|---|
| Polysaccharides (vegetable, animal, microbial, algae) | Starch and derivatives |
| | Cellulose and derivatives |
| | Chitin and chitosan |
| | Heparin |
| | Hyaluronic acid |
| | Gellan |
| | Alginic acid |
| | Xanthan |
| | Dextran |
| | Pullulan |
| | Pectin |
| | Agar |
| | Gums |
| Proteins | Albumin |
| | Casein |
| | Collagen/gelatin |
| | Fibrinogen/fibrin |
| | Wheat gluten, soy protein |
| | Zein (corn protein) |
| | Silk |
| Polyesters | Polylactic acid |
| | Polyhydroxyalkanoates |
| Polyphenols | Lignin |
| | Tannin |
| | Humic acid |
| Lipids | Waxes |
| | Surfactants |
| Specialty polymers | Shellac |
| | Natural rubber |
| | Nylon (from castor oil) |

[a]URL1; URL2; Briassoulis (2004).

versatile biopolymer with immense potential and low price for use in the nonfood industries (Choi et al., 1999; Mohanty et al., 2000). Starch constitutes more than 60% of cereal kernels and is relatively easy to separate from the other chemical components. These other components (fibers, protein, and fat) have a market value of their own as food or feed (Rexen et al., 1988). Starch is derived from renewable resources and is suitable for industrial applications. Every year nearly 20% of the starch produced in Europe is consumed by nonfood industries (Poutanen and Forsell, 1994). Moreover, the use of starch in plastic materials would reduce dependence on synthetic polymers made from imported oil and offers socioeconomic benefits because it generates rural jobs and a nonfood agricultural-based economy (Dufresne et al., 2000). The bioplastics found in the market are made mainly from starch. Starch-based bioplastics represent 85–90% of market's bioplastics (Bastioli, 2000). Among starch bioplastics are those manufactured with native or slightly modified starches, either isolated or blended with natural or synthetic molecules (Vilpoux and Avérous, 2004).

On the other hand, cellulose is the most abundant natural polymer, with wood as the greatest source. It is the main component (40–50% or more) of lignocellulose fibers, the other two being hemicellulose (20–30%) and lignin (10–30%). The purest form of cellulose sources is cotton linters (85–95%). Others are jute, kenaf, and chanvre (60–75%), as well as woods (40–50%) (URL2). Cellulose, starch, and their constituents are the two most important raw materials for the preparation of films (Engelhardt, 1995). Blends of starch and certain synthetic polymers or cellulose derivatives hold the lead among some new materials that have been used successfully (Ramkumar et al., 1996).

## 2.2  STARCH AND STARCH DERIVATIVES

Starch is a highly hydrophilic material that contains anhydroglucose units linked by $\alpha$-D-1,4-glycosidic bonds. The water absorbed by starch granules is mainly bound in the amorphous phase. At certain temperatures, shear stress, and pressure in an extruder the gelatinization processing disrupts the crystalline and ordered structure in starch granules to produce an amorphous phase (Yu et al., 2007). Starch granules vary in size from about 2 mm to 150 mm (Kerr, 1950). Pure starch, as distinct from commercial starch, is a white, odorless, tasteless, neutral powder, insoluble in cold water or organic solvents (Radley, 1953). Most starch granules are composed of a mixture of two polymers (Ahmad et al., 1999), namely, amylose and amylopectin. The amylose content can vary over a broad range, from 0% to about 75%, but typically is 20–25% (w/w) (Orford et al., 1987; Parker and Ring, 1996). In addition, starch is easily hydrolyzed to fermentable substrates (Rexen et al., 1988).

Starch is mostly water soluble, difficult to process, and brittle when used without the addition of a plasticizer. In addition, its mechanical properties are very sensitive to moisture content, which is difficult to control. In principle, some properties of starch can be significantly improved by blending it with synthetic polymers (Dufresne et al., 2000). Starch alone cannot form films with satisfactory mechanical properties (high percentage elongation and tensile and flexural strength) unless it is plasticized,

blended with other materials, chemically modified, or modified with a combination of these treatments (Liu, 2006).

Starch derivatives include dextrins, starch esters, and starch ethers. The starch esters most commonly used are esters with phosphoric acid (phosphate starches) and acetic acid (acetyl starches). The three most important starch ethers are the hydroxyethyl, hydroxypropyl, and carboxymethyl starches. Starch derivatives based on esters can be biologically reduced, while starches based on ethers are more difficult to biodegrade. However, the great variety of possible chemical modifications makes it possible to produce good slashing agents, which can be nearly completely biodegraded (URL3).

### 2.2.1 Thermoplastic-like Starch (or Destructurized Starch)

Thermoplastic-like starch (TPS) is a relatively new concept and, today, is one of the main research avenues for the manufacturing of biodegradable materials (Curvelo et al., 2001). The starch is not a true thermoplastic, but, in the presence of a plasticizer (water, glycerin, sorbitol, etc.), high temperature (90–180°C), and shearing, it melts and fluidizes, enabling its use in injection, extraction, and blowing equipment, such as that used for synthetic plastics (Lourdin et al., 1999). Unfortunately, TPS shows some drawbacks such as a strong hydrophilic character (water sensitivity), rather poor mechanical properties compared with conventional polymers, and an important postprocessing variation of its properties (Avérous and Boquillon, 2004).

The main use of destructurized starch alone is in soluble compostable foams such as loose fills, expanded trays, shape-molded parts, and expanded sheets and as a replacement for expanded polystyrene (Fang and Fowler, 2003).

### 2.2.2 Mechanical Properties

Avérous and Boquillon (2004) investigated the thermal and mechanical behavior of two different plasticized starch matrixes (TPS$_1$: dried wheat starch [70 wt%], glycerol [18 wt%] and water [12 wt%]; TPS$_2$: dried wheat starch [65 wt%] and glycerol [35 wt%]). The elongation at break was 124% for TPS$_1$ and 60% for TPS$_2$. The maximum tensile stress was 3.6 MPa and 1.4 MPa for TPS$_1$ and TPS$_2$, respectively, and the tensile modulus was 87 MPa for TPS$_1$, and 12 MPa for TPS$_2$. It can be concluded that the less plasticized matrix shows higher mechanical behavior. Avérous et al. (2001b) reported that the tensile modulus and strength of plasticized wheat starch (PWS) were 52 MPa and 3 MPa, respectively, and the elongation at break was 126%. According to Avérous et al. (2001a), the tensile strength and modulus of TPS were 3.6 MPa and 87 MPa, respectively, and the elongation at break was 124%.

Starch acetate was blended with corn stalk fibers at different concentrations (0%, 2%, 6%, 10%, and 14% w/w) for the production of biodegradable extruded foams. The results showed that the force required to shear the extrudates increased with increase in fiber content from 1% to 10%. There was a drastic increase in the force (0.06–0.075 N/mm$^2$) required to shear the extrudates with 14% fiber content (Ganjyal et al., 2004).

Dufresne et al. (2000) examined the mechanical behavior of an unfilled starch–glycerol matrix at room temperature as a function of glycerol content and relative humidity (RH). With increasing glycerol content, a decrease in the modulus was observed regardless of RH. This decrease was linear up to ∼15% glycerol. At higher glycerol content the drop in modulus was strongly increased.

The tensile modulus of unfilled starch–glycerol matrix films ranged between 0.24 and 20 MPa depending on the water content. The 35% RH conditioned sample displayed a typical rubberlike behavior with a high strain at break (∼140%). As the water content increased, starch showed a tendency to crystallize, and the elongation at break decreased strongly (by up to 18% at 43% RH). No significant difference was reported for more moist specimens. The strength of the material was almost moisture independent and ranged between 0.25 and 1 MPa (Anglés and Dufresne, 2001).

The mechanical properties of starch are presented in Table 2-2.

### 2.2.3  Thermal Properties

In the experiment conducted by Avérous and Boquillon (2004) (see above), the glass transition temperature ($T_g$) (by differential scanning calorimetry [DSC] analysis) was $87°C$ for $TPS_1$ and $12°C$ for $TPS_2$. In contrast, Avérous and Fringant (2001) found that the $T_g$ of various TPS formulations was below ambient temperature except for the 74% starch/10% glycerol/16% water blend.

Native starch (NS) was extracted from natural corn grain or from alkaline temperature-treated corn (ATS) ($95°C/40$ min in a 10% lime solution). The NS and the ATS starches were stored ($30°C$) at different relative humidities (%RH) (i.e., $11–84\%$). The $T_g$ and melting temperature ($T_m$) (by DSC) of the starches were determined at different storage times. The $T_g$ of the starches in 80% water dispersion was between 60 and $65°C$ (see Table 2-3).

### 2.3  CELLULOSE AND CELLULOSE DERIVATIVES

Cellulose is made up of glucopyranose units in β-(1–4) linkages (Kennedy et al., 1985). Sodium carboxymethyl cellulose (CMC) is the only water-soluble cellulose derivative used as a sizing agent (URL3). It is known that native celluloses, when subjected to strong acid hydrolysis, can readily break down into "microcrystalline cellulose" (MCC) with almost no weight loss (Battista, 1975; Ebeling et al., 1999).

Cellulose derivatives can be made by etherification, esterification, crosslinking, or graft-copolymerization reactions. Cellulose acetate is an important organic ester of cellulose. Cellulose ethers comprise methylcellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, and their derivatives (Hon, 2006). CMC is the largest industrial cellulose ether in terms of annual production (Richardson and Gorton, 2003). CMC is produced by reacting cellulose with sodium hydroxide and sodium chloroacetate, whereby the cellulose polymer is also depolymerized. CMC

**TABLE 2-2 Mechanical Properties of Starch–Cellulose Blends**

| Components | % Elongation | Tensile Strength (MPa) | Tensile Modulus (MPa) | References |
|---|---|---|---|---|
| 100% Plasticized starch films/ 0% cellulose crystallites | 110 | 2.6 | 40 | Lu et al. (2005) |
| 90% Plasticized starch films/ 10% cellulose crystallites | 85 | 5.7 | 130 | |
| 80% Plasticized starch films/ 20% cellulose crystallites | 73 | 6.5 | 260 | |
| 70% Plasticized starch films/ 30% cellulose crystallites | 47 | 7.7 | 310 | |
| 47.5% Corn starch/47.5% MCC/ 0% glycerol/5% water | 2.3 | 90 | 158.9 | Psomiadou et al. (1996) |
| 42.5% Corn starch/42.5% MCC/ 10% glycerol/5% water | 4.4 | 66.3 | 124.2 | |
| 34% Corn starch/34% MCC/ 27% glycerol/5% water | 8.5 | 55.0 | 53.4 | |
| 45% Corn starch/45% MCC/ 5% sorbitol/5% water | 4.1 | 73.3 | 131.5 | |
| 39.5% Corn starch/39.5% MCC/ 16% sorbitol/5% water | 6.0 | 48.9 | 94.2 | |
| 33.5% Corn starch/33.5% MCC/ 28% sorbitol/5% water | 9.3 | 18.3 | 40.0 | |
| 44.5% Corn starch/44.5% MCC/ 6% sucrose/5% water | 2.9 | 65.0 | 120.5 | |
| 40% Corn starch/40% MCC/ 15% sucrose/5% water | 3.5 | 43.4 | 82.7 | |
| 34.5% Corn starch/34.5% MCC/ 26% sucrose/5% water | 3.1 | 21.0 | 33.5 | |

| Material | | | | Reference |
|---|---|---|---|---|
| 45% Corn starch/45% MCC/ 5% xylose/5% water | 3.6 | 63.9 | 119.6 | |
| 39.5% Corn starch/39.5% MCC/ 16% xylose/5% water | 5.6 | 41.7 | 81.2 | |
| 35% Corn starch/35% MCC/ 25% xylose/5% water | 8.8 | 20.5 | 34.7 | Lee et al. (2006) |
| Cellulose diacetate | 4 | 22 | 6254 | |
| 10% starch/90% plasticized cellulose diacetate | 6 | 49.0 | 1727 | |
| 20% starch/80% plasticized cellulose diacetate | 10 | 44.0 | 1551 | |
| 30% starch/70% plasticized cellulose diacetate | 12 | 26.0 | 1064 | |
| 40% starch/60% plasticized cellulose diacetate | 15 | 23.0 | 953 | |
| 50% starch/50% plasticized cellulose diacetate | 18 | 16.0 | 858 | |
| CP (clear-pure) cellulose acetate propionate | 50 | 41.3 | 1241 | URL5 |
| Cellulose acetate plastic nanocomposites (Process A, 0% clay) | 24 | 26 | 1300 | Wibowo et al. (2006) |
| Cellulose acetate plastic nanocomposites (Process A, 5% clay) | 20 | 27 | 1500 | |
| Cellulose acetate plastic nanocomposites (Process B, 0% clay) | 14 | 32 | 2100 | |
| Cellulose acetate plastic nanocomposites (Process B, 5% clay) | 15 | 44 | 2800 | |
| 100% Plasticized starch films/0% ramie cellulose nanocrystallites | 95 | 2.8 | 60 | Lu et al. (2006) |

(*Continued*)

**TABLE 2-2** *Continued*

| Components | % Elongation | Tensile Strength (MPa) | Tensile Modulus (MPa) | References |
|---|---|---|---|---|
| 90% Plasticized starch films/10% ramie cellulose nanocrystallites | 70 | 5.3 | 160 | Cao et al. (2006) |
| 80% Plasticized starch films/20% ramie cellulose nanocrystallites | 60 | 5.5 | 240 | |
| 70% Plasticized starch films/30% ramie cellulose nanocrystallites | 30 | 6.1 | 450 | |
| 60% Plasticized starch films/40% ramie cellulose nanocrystallites | 15 | 7.0 | 510 | |
| 0% Benzyl starch/100% regenerated cellulose | 8 | 66 | – | |
| 10% Benzyl starch/90% regenerated cellulose | 9 | 72 | – | |
| 20% Benzyl starch/80% regenerated cellulose | 6 | 76 | – | |
| 30% Benzyl starch/70% regenerated cellulose | 7 | 78 | – | |
| 40% Benzyl starch/60% regenerated cellulose | 6.5 | 80 | – | |
| 50% Benzyl starch/50% regenerated cellulose | 9.5 | 93 | – | |
| 60% Benzyl starch/40% regenerated cellulose | 14 | 102 | – | |
| 70% Benzyl starch/30% regenerated cellulose | 12 | 103 | – | |
| 100% Plasticized starch/0% tunicin[a] whiskers | 0 (35% RH) | 0 (35% RH) | 1.4 (35% RH) | Anglés and Dufresne (2001) |
| | 20 (75% RH) | 1 (75% RH) | 0.1 (75% RH) | |

| Material | | | | Reference |
|---|---|---|---|---|
| 95% Plasticized starch/5% tunicin whiskers | 40 (35% RH)<br>20 (75% RH) | 4 (35% RH)<br>1 (75% RH) | 0.7 (35% RH)<br>0.2 (75% RH) | Avérous et al. (2001b) |
| 90% Plasticized starch/10% tunicin whiskers | 50 (35% RH)<br>30 (75% RH) | 4.5 (35% RH)<br>1 (75% RH) | 0.6 (35% RH)<br>0.15 (75% RH) | |
| 85% Plasticized starch/15% tunicin whiskers | 60 (35% RH)<br>30 (75% RH) | 5 (35% RH)<br>1.5 (75% RH) | 0.55 (35% RH)<br>0.1 (75% RH) | |
| 80% Plasticized starch/20% tunicin whiskers | 120 (35% RH)<br>40 (75% RH) | 9 (35% RH)<br>1.5 (75% RH) | 0.5 (35% RH)<br>0.1 (75% RH) | |
| 75% Plasticized starch/25% tunicin whiskers | 320 (35% RH)<br>50 (75% RH) | 15 (35% RH)<br>1 (75% RH) | 0.4 (35% RH)<br>0.1 (75% RH) | |
| Plasticized wheat starch (PWS) | 126 (50% RH) | 3 (50% RH) | 52 (50% RH) | |
| 85% PWS/15% B400 | 31 (50% RH) | 13 (50% RH) | 430 (50% RH) | |
| 70% PWS/30% B400 | 19 (50% RH) | 22 (50% RH) | 670 (50% RH) | |
| 85% PWS/15% BC200 | 33 (50% RH) | 10 (50% RH) | 350 (50% RH) | |
| 70% PWS/30% BC200 | 19 (50% RH) | 15 (50% RH) | 630 (50% RH) | |
| 85% PWS/15% B600 | 47 (50% RH) | 7 (50% RH) | 296 (50% RH) | |
| 70% PWS/30% B600 | 10 (50% RH) | 13 (50% RH) | 757 (50% RH) | |
| PWS 1 (reference) | 3 (50% RH) | 25 (50% RH) | 1110 (50% RH) | |
| PWS 1 (reference) | 60 (75% RH) | 3 (75% RH) | 100 (75% RH) | |
| PWS 2/20% cellulose fibers | 8 (50% RH) | 26 (50% RH) | 1150 (50% RH) | |
| PWS 2/20% cellulose fibers | n.d. (75% RH) | n.d. (75% RH) | n.d. (75% RH) | |
| PWS 3/30% cellulose fibers | 6 (50% RH) | 24 (50% RH) | 1280 (50% RH) | |
| PWS 3/30% cellulose fibers | 15 (75% RH) | 7 (75% RH) | 200 (75% RH) | |
| 90% Soluble starch/0% methyl cellulose/10% water | 4.2 | 50.5 | – | Arvanitoyannis and Biliaderis (1999) |
| 70% Soluble starch/20% methyl cellulose/10% water | 8 | 33.2 | – | |
| 50% Soluble starch/40% methyl cellulose/10% water | 10.6 | 12.6 | – | |

**TABLE 2-2** *Continued*

| Components | % Elongation | Tensile Strength (MPa) | Tensile Modulus (MPa) | References |
|---|---|---|---|---|
| 45% Soluble starch/45% methyl cellulose/10% water | 8.9 | 61.2 | – | |
| 40% Soluble starch/40% methyl cellulose/20% water | 16.7 | 49.5 | – | |
| 35% Soluble starch/35% methyl cellulose/30% water | 24.5 | 38.7 | – | |
| 45% Corn starch/45% methyl cellulose/5% glycerol/5% water | 11.9 | 59.4 | – | |
| 40% Corn starch/40% methyl cellulose/15% glycerol/5% water | 25.3 | 43.3 | – | |
| 32.5% Corn starch/32.5% methyl cellulose/30% glycerol/5% water | 34.2 | 33.5 | – | |
| 45% Corn starch/45% methyl cellulose/5% sorbitol/5% water | 14.3 | 54.6 | – | |
| 40% Corn starch/40% methyl cellulose/15% sorbitol/5% water | 28.7 | 35.2 | – | |
| 32.5% Corn starch/32.5% methyl cellulose/30% sorbitol/5% water | 39.4 | 28.4 | – | |
| 45% Corn starch/45% methyl cellulose/5% xylose/5% water | 8.8 | 48.4 | – | |
| 40% Corn starch/40% methyl cellulose/15% xylose/5% water | 21.5 | 32.5 | – | |
| 32.5% Corn starch/32.5% methyl cellulose/30% xylose/5% water | 28.4 | 25.6 | – | |
| $TPS_1$ (dried wheat starch [70 wt%], glycerol [18 wt%] and water [12 wt%]) | 124 | 3.6 | 87 | Avérous and Boquillon (2004) |

| Material | | | | Reference |
|---|---|---|---|---|
| TPS$_2$ (dried wheat starch [65 wt%] and glycerol [35 wt%]) | 60 | 1.4 | 12 | Avérous et al. (2001a) |
| TPS | 124 | 3.6 | 87 | Dufresne et al. (1999) |
| 100% Starch/0% glycerol | – | – | 2000 (25% RH) 1700 (58% RH) 1600 (75% RH) | |
| 90% Starch/10% glycerol | – | – | 1900 (25% RH) 1600 (58% RH) 1500 (75% RH) | |
| 80% Starch/20% glycerol | – | – | 1250 (25% RH) 750 (58% RH) 500 (75% RH) | |
| 70% Starch/30% glycerol | – | – | 250 (25% RH) 250 (58% RH) 250 (75% RH) | |
| 100% Starch/0% cellulose microfibrils/ 0% glycerol | – | – | 2200 (25% RH) 1900 (58% RH) 1800 (75% RH) | |
| 90% Starch/10% cellulose microfibrils/ 0% glycerol | – | – | 3500 (25% RH) 3000 (58% RH) 2800 (75% RH) | |
| 80% Starch/20% cellulose microfibrils/ 0% glycerol | – | – | 4500 (25% RH) 3500 (58% RH) 3500 (75% RH) | |
| 70% Starch/30% cellulose microfibrils/ 0% glycerol | – | – | 5400 (25% RH) 4500 (58% RH) 4500 (75% RH) | |
| 85% Starch/0% cellulose microfibrils/ 15% glycerol | – | – | 2000 (25% RH) 1800 (58% RH) | |

**TABLE 2-2**  *Continued*

| Components | % Elongation | Tensile Strength (MPa) | Tensile Modulus (MPa) | References |
|---|---|---|---|---|
| 75% Starch/10% cellulose microfibrils/ 15% glycerol | – | – | 1000 (75% RH)<br>1700 (25% RH)<br>2100 (58% RH)<br>2000 (75% RH) | |
| 65% Starch/20% cellulose microfibrils/ 15% glycerol | – | – | 4000 (25% RH)<br>2600 (58% RH)<br>2100 (75% RH) | |
| 55% Starch/30% cellulose microfibrils/ 15% glycerol | – | – | 4000 (25% RH)<br>3000 (58% RH)<br>2500 (75% RH) | |
| 70% Starch/0% cellulose microfibrils/ 30% glycerol | – | – | 400 (25% RH)<br>100 (58% RH)<br>0 (75% RH) | |
| 60% Starch/10% cellulose microfibrils/ 30% glycerol | – | – | 1000 (25% RH)<br>700 (58% RH)<br>500 (75% RH) | |
| 50% Starch/20% cellulose microfibrils/ 30% glycerol | – | – | 2000 (25% RH)<br>1700 (58% RH)<br>1000 (75% RH) | |
| 40% Starch/30% cellulose microfibrils/ 30% glycerol | – | – | 2500 (25% RH)<br>2000 (58% RH)<br>1100 (75% RH) | |

[a]Tunicin: animal cellulose.

**TABLE 2-3  Glass Transition Temperatures ($T_g$) of Starch–Cellulose Blends**

| Components | $T_g$ (°C) | Method of $T_g$ Determination | References |
|---|---|---|---|
| 100% Plasticized starch films/0% cellulose nanocrystallites | 23 | DSC | Lu et al. (2005) |
| 90% Plasticized starch films/10% cellulose nanocrystallites | 30 | DSC | |
| 80% Plasticized starch films/20% cellulose nanocrystallites | 40 | DSC | |
| 70% Plasticized starch films/30% cellulose nanocrystallites | 48 | DSC | |
| 100% Plasticized starch films/0% cellulose nanocrystallites | 25 | DMTA | |
| 90% Plasticized starch films/10% cellulose nanocrystallites | 45 | DMTA | |
| 80% Plasticized starch films/20% cellulose nanocrystallites | 40 | DMTA | |
| 70% Plasticized starch films/30% cellulose nanocrystallites | 50 | DMTA | |
| 47% Corn starch/47% methyl cellulose/6% water | 110.9 | DTA (2nd run) | Arvanitoyannis (1999); Psomiadou et al. (1996) |
| 45% Corn starch/45% methyl cellulose/10% water | 92.2 | DTA (2nd run) | |
| 42% Corn starch/42% methyl cellulose/16% water | 67.3 | DTA (2nd run) | |
| 39% Corn starch/39% methyl cellulose/22% water | 49.8 | DTA (2nd run) | |

*(Continued)*

**TABLE 2-3** *Continued*

| Components | $T_g$ (°C) | Method of $T_g$ Determination | References |
|---|---|---|---|
| 37% Corn starch/37% methyl cellulose/ 26% water | 34.5 | DTA (2nd run) | |
| 35% Corn starch/35% methyl cellulose/ 30% water | 17.1 | DTA (2nd run) | |
| 78% Corn starch/5% methyl cellulose/ 17% water | 58.3 | DTA (2nd run) | |
| 58% Corn starch/25% methyl cellulose/ 17% water | 65.2 | DTA (2nd run) | |
| 28% Corn starch/55% methyl cellulose/ 17% water | 77.0 | DTA (2nd run) | |
| 47% Corn starch/47% methyl cellulose/ 6% water | 109.4 | DMTA ($E'$) | |
| 45% Corn starch/45% methyl cellulose/ 10% water | 91.5 | DMTA ($E'$) | |
| 42% Corn starch/42% methyl cellulose/ 16% water | 68.4 | DMTA ($E'$) | |
| 39% Corn starch/39% methyl cellulose/ 22% water | 48.5 | DMTA ($E'$) | |
| 37% Corn starch/37% methyl cellulose/ 26% water | 36.7 | DMTA ($E'$) | |
| 35% Corn starch/35% methyl cellulose/ 30% water | 18.5 | DMTA ($E'$) | |
| 78% Corn starch/5% methyl cellulose/ 17% water | 59.5 | DMTA ($E'$) | |
| 58% Corn starch/25% methyl cellulose/ 17% water | 67.1 | DMTA ($E'$) | |
| 28% Corn starch/55% methyl cellulose/ 17% water | 76.1 | DMTA ($E'$) | |

| Composition | Value | Method |
|---|---|---|
| 47% Corn starch/47% methyl cellulose/6% water | 123.6 | DMTA (tan δ) |
| 45% Corn starch/45% methyl cellulose/10% water | 110.2 | DMTA (tan δ) |
| 42% Corn starch/42% methyl cellulose/16% water | 79.6 | DMTA (tan δ) |
| 39% Corn starch/39% methyl cellulose/22% water | 63.5 | DMTA (tan δ) |
| 37% Corn starch/37% methyl cellulose/26% water | 45.6 | DMTA (tan δ) |
| 35% Corn starch/35% methyl cellulose/30% water | 23.0 | DMTA (tan δ) |
| 78% Corn starch/5% methyl cellulose/17% water | 62.8 | DMTA (tan δ) |
| 58% Corn starch/25% methyl cellulose/17% water | 76.0 | DMTA (tan δ) |
| 28% Corn starch/55% methyl cellulose/17% water | 89.3 | DMTA (tan δ) |
| 47.5% Corn starch/47.5% MCC/0% glycerol/5% water | 118.5 | DTA |
| 42.5% Corn starch/42.5% MCC/10% glycerol/5% water | 59.4 | DTA |
| 38% Corn starch/38% MCC/19% glycerol/5% water | −2.8 | DTA |
| 45% Corn starch/45% MCC/5% sorbitol/5% water | 91.8 | DTA |
| 42.5% Corn starch/42.5% MCC/10% sorbitol/5% water | 57.0 | DTA |
| 39.5% Corn starch/39.5% MCC/16% sorbitol/5% water | 23.8 | DTA |
| 44.5% Corn starch/44.5% MCC/6% sucrose/5% water | 87.4 | DTA |

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**TABLE 2-3** *Continued*

| Components | $T_g$ (°C) | Method of $T_g$ Determination | References |
|---|---|---|---|
| 40% Corn starch/40% MCC/15% sucrose/ 5% water | 19.1 | DTA | |
| 37.5% Corn starch/37.5% MCC/ 20% sucrose/5% water | −10.0 | DTA | |
| 45% Corn starch/45% MCC/5% xylose/ 5% water | 84.2 | DTA | |
| 39.5% Corn starch/39.5% MCC/ 16% xylose/5% water | 11.3 | DTA | |
| 37.5% Corn starch/37.5% MCC/ 20% xylose/5% water | −8.5 | DTA | |
| 47.5% Corn starch/47.5% MCC/ 0% glycerol/5% water | 113.4 | DMTA ($E'$) | |
| 42.5% Corn starch/42.5% MCC/ 10% glycerol/5% water | 52.3 | DMTA ($E'$) | |
| 38% Corn starch/38% MCC/ 19% glycerol/5% water | −5.1 | DMTA ($E'$) | |
| 45% Corn starch/45% MCC/5% sorbitol/ 5% water | 84.1 | DMTA ($E'$) | |
| 42.5% Corn starch/42.5% MCC/ 10% sorbitol/5% water | 48.0 | DMTA ($E'$) | |
| 39.5% Corn starch/39.5% MCC/ 16% sorbitol/5% water | 17.8 | DMTA ($E'$) | |
| 44.5% Corn starch/44.5% MCC/ 6% sucrose/5% water | 80.1 | DMTA ($E'$) | |
| 40% Corn starch/40% MCC/15% sucrose/ 5% water | 11.8 | DMTA ($E'$) | |
| 37.5% Corn starch/37.5% MCC/ 20% sucrose/5% water | −22.5 | DMTA ($E'$) | |

| Material | Value | Method | Reference |
|---|---|---|---|
| 45% Corn starch/45% MCC/5% xylose/5% water | 77.1 | DMTA ($E'$) | |
| 39.5% Corn starch/39.5% MCC/16% xylose/5% water | 7.4 | DMTA ($E'$) | |
| 37.5% Corn starch/37.5% MCC/20% xylose/5% water | −14.5 | DMTA ($E'$) | |
| 47.5% Corn starch/47.5% MCC/0% glycerol/5% water | 130.0 | DMTA (tan δ) | |
| 42.5% Corn starch/42.5% MCC/10% glycerol/5% water | 70.3 | DMTA (tan δ) | |
| 38% Corn starch/38% MCC/19% glycerol/5% water | 6.8 | DMTA (tan δ) | |
| 45% Corn starch/45% MCC/5% sorbitol/5% water | 97.5 | DMTA (tan δ) | |
| 42.5% Corn starch/42.5% MCC/10% sorbitol/5% water | 66.9 | DMTA (tan δ) | |
| 39.5% Corn starch/39.5% MCC/16% sorbitol/5% water | 30.3 | DMTA (tan δ) | |
| 44.5% Corn starch/44.5% MCC/6% sucrose/5% water | 93.5 | DMTA (tan δ) | |
| 40% Corn starch/40% MCC/15% sucrose/5% water | 58.3 | DMTA (tan δ) | |
| 37.5% Corn starch/37.5% MCC/20% sucrose/5% water | −4.5 | DMTA (tan δ) | |
| 45% Corn starch/45% MCC/5% xylose/5% water | 88.0 | DMTA (tan δ) | |
| 39.5% Corn starch/39.5% MCC/16% xylose/5% water | 17.3 | DMTA (tan δ) | |
| 37.5% Corn starch/37.5% MCC/20% xylose/5% water | −1.2 | DMTA (tan δ) | |
| Cellulose diacetate | 114.3 | – | Lee et al. (2006) |

**TABLE 2-3** *Continued*

| Components | $T_g$ (°C) | Method of $T_g$ Determination | References |
|---|---|---|---|
| 10% Starch/80% plasticized cellulose diacetate | 111.9 | – | |
| 20% Starch/80% plasticized cellulose diacetate | 101.7 | – | |
| 30% Starch/70% plasticized cellulose diacetate | 98.8 | – | |
| 40% Starch/60% plasticized cellulose diacetate | 95.2 | – | |
| 50% Starch/50% plasticized cellulose diacetate | 91.5 | – | |
| CP (clear–pure) cellulose | 130 | DSC | Glasser et al. (2000) |
| Cellulose propionate difluoroethoxy acetate | 67 | DSC | |
| Cellulose octafluoropentoxy acetate | 113 | DSC | |
| Cellulose propionate octafluoropentoxy acetate | 53 | DSC | |
| Medium–high DS hydroxypropyl cellulose | 105 | Oscillatory rheometry | Gómez-Carracedo et al. (2003) |
| Hydroxypropylmethyl cellulose | 170–198 | Oscillatory rheometry | |
| Methylcellulose | 184–197 | Oscillatory rheometry | |
| Low DS hydroxypropyl cellulose | 220 | Oscillatory rheometry | |
| Plasticized wheat starch | 31 | DMTA (tanδ) | Avérous et al. (2001b) |
| PWS/cellulose fibers | 59–64 | DMTA (tan δ) | |

| Composition | Value | Method | Reference |
| --- | --- | --- | --- |
| 74% Starch/10% glycerol/26% water | 43 | DSC | Avérous and Fringant (2001) |
| 70% Starch/18% glycerol/12% water | 8 | DSC | |
| 67% Starch/24% glycerol/9% water | −7 | DSC | |
| 65% Starch/35% glycerol/0% water | −20 | DSC | |
| 45% Corn starch/45% methyl cellulose/0% glycerol/10% water | 84.9 | DTA | Arvanitoyannis and Biliaderis (1999) |
| 42.5% Corn starch/42.5% methyl cellulose/5% glycerol/10% water | 56.8 | DTA | |
| 37.5% Corn starch/37.5% methyl cellulose/15% glycerol/10% water | 22.9 | DTA | |
| 30% Corn starch/30% methyl cellulose/30% glycerol/10% water | – | DTA | |
| 42.5% Corn starch/42.5% methyl cellulose/5% sorbitol/10% water | 43.9 | DTA | |
| 37.5% Corn starch/37.5% methyl cellulose/15% sorbitol/10% water | 17.6 | DTA | |
| 30% Corn starch/30% methyl cellulose/30% sorbitol/10% water | – | DTA | |
| 42.5% Corn starch/42.5% methyl cellulose/5% xylose/10% water | 48.0 | DTA | |
| 37.5% Corn starch/37.5% methyl cellulose/15% xylose/10% water | 21.3 | DTA | |
| 100% Plasticized starch/0% tunicin whiskers | 13.2 (0% RH) | DSC | Mathew and Dufresne (2002) |
| 95% Plasticized starch/5% tunicin whiskers | 16.3 (0% RH) | DSC | |
| 90% Plasticized starch/10% tunicin whiskers | 18.7 (0% RH) | DSC | |
| 85% Plasticized starch/15% tunicin whiskers | 17.9 (0% RH) | DSC | |

*(Continued)*

**TABLE 2-3** *Continued*

| Components | $T_g$ (°C) | Method of $T_g$ Determination | References |
|---|---|---|---|
| 75% Plasticized starch/25% tunicin whiskers | 10.5 (0% RH) | DSC | |
| 100% Plasticized starch/0% tunicin whiskers | −30.3 (58% RH) | DSC | |
| 95% Plasticized starch/5% tunicin whiskers | −31.5 (58% RH) | DSC | |
| 90% Plasticized starch/10% tunicin whiskers | −32.0 (58% RH) | DSC | |
| 85% Plasticized starch/15% tunicin whiskers | −25.1 (58% RH) | DSC | |
| 75% Plasticized starch/25% tunicin whiskers | −34.5 (58% RH) | DSC | |
| 100% Plasticized starch/0% tunicin whiskers | −64.7 (98% RH) | DSC | |
| 95% Plasticized starch/5% tunicin whiskers | −61.6 (98% RH) | DSC | |
| 90% Plasticized starch/10% tunicin whiskers | −56.5 (98% RH) | DSC | |
| 85% Plasticized starch/15% tunicin whiskers | −49.2 (98% RH) | DSC | |
| 75% Plasticized starch/25% tunicin whiskers | −54.5 (98% RH) | DSC | |

is the preferred additive for increasing the adhesion of starch sizes for cotton. However, CMC must be classed as being very difficult to degrade. Only 20% of the initial amount is eliminated after 7 days. However, it is also reported that CMC can be reduced after long periods of adaptation ($>$4 weeks) and favorable conditions (especially higher temperatures) (URL3).

### 2.3.1  Mechanical Properties

Pure cellulose diacetate (CDA) has a tensile strength of 62 MPa and an elongation of 4%. The glass transition temperature of pure CDA was higher than that of plasticized CDA (Lee et al., 2006). Wibowo et al. (2006) examined the mechanical properties of biodegradable nanocomposites from cellulose acetate. Two methods of composite processing were used: Process A (extrusion at 200 rpm, followed by compression molding) and Process B (extrusion at 200 rpm, followed by injection molding). In both methods 0% and 5% (wt) clay was added to fabricated cellulose acetate plastic matrix. An increase of 60% in tensile strength and 80% in tensile modulus was reported for Process B samples compared to Process A samples. Furthermore, an increase of 38% in tensile strength and 33% in tensile modulus was observed for nanocomposites with 5% (wt) clay reinforcement compared to that of matrix in Process B.

Samples of commercial cleanex (fibrous delignified native cellulose) were pressed and annealed together with unpressed ones for 6 h at 120–265°C. An increase in tensile strength and tensile modulus of the pressed cleanex annealed at 180–230°C was observed, while a decrease of these parameters was reported when the annealing temperature was 265°C. Maximum values of tensile strength of 3.9 MPa and tensile modulus of 182 MPa were obtained after annealing under pressure at 230°C. The values of tensile strength and tensile modulus decreased continuously in the case of unpressed cleanex annealed at 120–265°C and they were lower than those of the pressed samples annealed at temperatures above 130°C (Avramova and Fakirov, 1990) (see Table 2-3).

### 2.3.2  Thermal Properties

The glass transitions of novel cellulose derivatives ranged between 53°C and 113°C, and are distinctly below that of cellulose propionate. The influence of the larger octa-fluoropentoxy group compared with the difluoroethoxy group is revealed by the significant $T_g$ reduction of 14°C (from 67°C to 53°C) (Glasser et al., 2000). Values of $T_g$ for various nonionic cellulose ethers were analyzed by DSC, modulated temperature differential scanning calorimetry (TMDSCO), and oscillatory rheometry. The best resolution was obtained using oscillatory rheometry since these cellulose ethers undergo considerable changes in their storage and loss moduli when reaching the $T_g$. Values of $T_g$ were in the order: medium–high DS (degree of substitution) hydroxypropyl cellulose 105°C $<$ hydroxypropylmethyl cellulose 170–198°C $<$ methyl cellulose 184–197°C $<$ low DS hydroxypropyl cellulose 220°C. For

hydroxypropylmethyl celluloses, the $T_g$ increases as the methoxyl/hydroxypropoxyl content ratio decreases (Gómez-Carracedo et al., 2003) (see Table 2-3).

## 2.4   STARCH–CELLULOSE BLENDS

In order to overcome the inherent hydrophilicity of starch, blends with conventional hydrophobic synthetic polymers have been considered for the production of plastic bags and commodity products (Corti et al., 1992). In order to reduce the sensitivity of starch to water, it is blended with more hydrophobic, thermoplastic materials such as polycaprolactone, polyhydroxybutyrate/valerate and cellulose acetate. Such blends are completely biodegradable under composting and other biologically active environments (Fang and Fowler, 2003). Both cellulose acetate and starch acetate have been known since the nineteenth century. However, a blend of these two common materials has not before been available because of processing problems (URL6).

### 2.4.1   Mechanical Properties

Natural cellulose fibers with different initial average lengths [60 (SF), 300 (MF) and 900 (LF) μm] and paper pulp fibers (PPF) were added to different plasticized starch matrixes (TPS$_1$ and TPS$_2$) (Avérous and Boquillon, 2004). When 10% of natural cellulose fibers with initial average lengths 60 (SF) and 300 (MF) was added to TPS$_1$ and TPS$_2$, the tensile modulus was greater and the elongation ratios were lower for TPS$_1$ than for TPS$_2$. On the other hand, the tensile modulus and the elongation ratios were greater when 20% of natural cellulose fibers [with initial average lengths 900 (LF) μm] and PPF was added to the TPS$_2$ than for the blend of 20% of natural cellulose fibers/PPF and TPS$_2$.

The tensile strength and Young's modulus of the plasticized starch (PS)/cellulose nanocrystallites and PS/ramie cellulose nanocrystallites (RN) increased significantly from 2.5 to 7.8 MPa and from about 36 to 301 MPa with increasing filler (RN) content from 0% to 30% (wt), whereas the elongation at break decreased from 105% to 46% (Lu et al., 2005, 2006).

The mechanical behavior of cellulose microfibril–plasticized starch composites was investigated by Dufresne et al. (2000). It was shown that cellulose microfibrils appreciably reinforce the starch matrix, regardless of the glycerol content. The evolution of the tensile modulus as a function of the cellulose content was nearly linear. In addition, the higher modulus was observed for the less plasticized material.

According to Psomiadou et al. (1996), with regard to mechanical properties the corn starch/methyl cellulose (MC)/water or polyol (glycerol, D-glucose, sucrose, xylose) blends exhibited similar behavior to the corn starch/MCC/water blends. Sucrose exerts an antiplasticizing action, resulting in considerably lower tensile strength and percentage elongation, whereas both sorbitol and glucose impart lower tensile strength but higher percentage elongation (plasticizing action). The incorporation of MC in the starch matrix was found to have a rather beneficial

effect resulting in a gradual increase of tensile strength and percentage elongation. When MCC was employed, the tensile strength increased but the percentage elongation increased only slightly.

Acetylated starch and 15% cellulose acetate were pretreated with acetone solution, and the pretreated mixture was extruded as a composite. The tensile strength was effectively improved due to addition of cellulose acetate compared with the acetylated starch plastic (Chen et al., 2003). A series of water-resistant cellulose films was prepared by coating castor oil-based polyurethane/benzyl starch (BS) semi-interpenetrating polymer networks. The tensile strength and elongation at break of cellulose-coated films increased simultaneously with the increasing BS concentration on the whole and reached maximum values of 102 MPa and 14%, respectively (Cao et al., 2006).

Lee et al. (2006) examined the mechanical properties of plasticized cellulose diacetate (CDA) and starch, which were prepared using melt processing methods with triacetine (TA) as the primary plasticizer and epoxidized soybean oil (ESO) as the secondary plasticizer. At 7% (wt) starch in a blend, the tensile strength decreased from 62 MPa to 49 MPa for pure CDA, and the elongation increased from 4% to 6% (wt). The tensile strength was 16 MPa with 18% elongation at a 35% (wt) starch content. In general, the tensile strength and Young's modulus decreased and the level of elongation increased with increasing starch content in the CDA matrix.

Arvanitoyannis and Biliaderis (1999) estimated the tensile strength and percentage elongation of polyol-plasticized edible blends (polyols: glycerol, sorbitol, xylose) made from soluble starch–MC at different water contents. Percentage elongation exhibited a considerable increase, up to three times the initial values, while the tensile strength dropped to lower than 50% of the original values.

The mechanical properties of plasticized wheat starch (PWS)/cellulose fibers were examined by Avérous et al. (2001b). The characteristics of the cellulose fibers were: B600 [fiber length ($L$) 60 $\mu$m, diameter ($d$) 20 $\mu$m, $L/d$ 3]; BC200 ($L$ 300 $\mu$m, $d$ 20 $\mu$m, $L/d$ 15); and B400 ($L$ 900 $\mu$m, $d$ 20 $\mu$m, $L/d$ 45). Young's modulus ($E$ modulus) was increased by a factor of 5–9 (order of magnitude). For the lowest fiber content (15%), the modulus increases with the fiber length. The best results are obtained with B400 fibers that have the greatest length. Strength improvement depends both on the fiber length and content. Elongation at break decreased with the addition of fiber.

Avérous et al. (2001a) investigated the potential effect of the addition of cellulose fibers in a TPS matrix and reported the subsequent properties. Modulus or maximum strength results showed a strong improvement on addition of fibers to the TPS matrix.

Anglés and Dufresne (2001) showed that no significant reinforcing effect was observed on the tensile modulus of glycerol-plasticized starch/tunicin whisker composite films regardless of the moisture content up to 16.2% (wt) tunicin whiskers. When the cellulose content reached 25% (wt) an increase in the modulus was observed. No significant evolution for either the tensile strength or the elongation at break was reported, regardless of the whisker loading. On the contrary, the strength of the composite conditioned at 35% RH increased as the cellulose content increased.

The mechanical behavior of plasticized wheat starches referred to as PWS 1 to 3 with increasing glycerol/starch ratios, i.e., 0.14, 0.26 and 0.54, respectively, at 50% and 70% RH was also investigated by Avérous et al. (2001b). At 50% RH, almost the same modulus is found for PWS 1 as for the system PWS 3 fibers. From 50% to 75% RH, the modulus of PWS 1 is decreased by a factor of 10, whereas that of the composites PWS 3 fibers is only reduced by a factor of 6. PWS 2 and 3 have similar tensile strength and modulus but very different impact strength resistance.

The mechanical properties of various starch–cellulose blends are shown in Table 2-2.

### 2.4.2  Thermal Properties

It is sometimes difficult to determine the glass transition of plasticized starch by DSC analysis because the heat capacity change is quite low at the glass transition. The $T_g$ determined by dynamic mechanical analysis (DMA) (tan $\delta$) was different from the $T_g$ determined by DSC. Dynamic mechanical thermal analysis (DMTA) determination is used to obtain this transition, which is clearly demonstrated by a broad tan $\delta$ peak. Tan $\delta$ drawing shows two relaxations ($\alpha$ and $\beta$). The main relaxation (termed $\alpha$), associated with a large tan $\delta$ peak and an important decrease of the storage modulus, can be attributed to the TPS glass relaxation (Avérous and Boquillon, 2004). After the addition of cellulose fibers to PWS, a shift of the glass transition temperature (DSC analysis) of the matrix toward higher temperatures was observed for reinforced materials (maximum of tan $\delta$ at 59–64°C instead of 31°C for PWS alone) (Avérous et al., 2001b).

Plasticized starch film exhibited the $T_g$ transition at about 22°C. The $T_g$ transition of the glycerol-rich phase of PS film/cellulose nanocrystallites ranged from $-80$°C to $-50$°C, but could not be determined because of the limitation of refrigerated cooling systems in DSC. By adding cellulose crystallites into starch matrix, the $T_g$ transition of the starch-rich phase is shifted to higher temperatures of 23–48°C (Lu et al., 2005). According to Lu et al. (2006), the PS film exhibited a $T_g$ transition at about 26.8°C. By incorporating RN fillers of 0–40% (wt) into PS, the $T_g$ transition for starch rich-phase is shifted to a higher temperature of 26.8–55.7°C.

The $T_g$ of cellulose microfibril–plasticized starch composites was decreased to temperatures lower than room temperature, and the effect of adding filler became more significant when the glycerol content was increased (Dufresne et al., 2000). An increase of the main $T_g$ of about 30°C was reported for the addition of cellulose fibers to the TPS matrix (Avérous et al., 2001a). Moreover, the presence of TA and ESO, as plasticizers, in CDA/starch decreased the $T_g$ of the composites (Lee et al., 2006).

Psomiadou et al. (1996) investigated the thermal properties of various aqueous blends of microcrystalline cellulose (MCC) or methyl cellulose (MC) and corn starch with or without polyols (glycerol, D-glucose, sucrose, xylose). The results showed that the higher the water content, the greater the depression of the $T_g$ value (DTA, DMTA, and permeability measurements).

**TABLE 2-4    Melting Temperatures ($T_m$) of Starch–Cellulose Blends**

| Components | $T_m$ (°C) | Conditions | References |
|---|---|---|---|
| 100% Plasticized starch/0% tunicin whiskers | 133.4 | 43% RH | Anglés and Dufresne (2001) |
| 96.8% Plasticized starch/3.2% tunicin whiskers | 132.9 | | |
| 93.8% Plasticized starch/6.2% tunicin whiskers | 131.9 | | |
| 83.3% Plasticized starch/ 16.7% tunicin whiskers | 132.9 | | |
| 75% Plasticized starch/25% tunicin whiskers | 135.4 | | |
| 100% Plasticized starch/0% tunicin whiskers | 157.9 | 58% RH | |
| 96.8% Plasticized starch/3.2% tunicin whiskers | 159.4 | | |
| 93.8% Plasticized starch/6.2% tunicin whiskers | 165.9 | | |
| 83.3% Plasticized starch/ 16.7% tunicin whiskers | 160.9 | | |
| 75% Plasticized starch/25% tunicin whiskers | 170.3 | | |
| 100% Plasticized starch/0% tunicin whiskers | 156.9 | 75% RH | |
| 96.8% Plasticized starch/3.2% tunicin whiskers | 156.9 | | |
| 93.8% Plasticized starch/6.2% tunicin whiskers | 156.9 | | |
| 83.3% Plasticized starch/ 16.7% tunicin whiskers | 157.4 | | |
| 75% Plasticized starch/25% tunicin whiskers | 159.4 | | |
| 100% Plasticized starch/0% tunicin whiskers | 146.5 | 43% RH | Mathew and Dufresne (2002) |
| 95% Plasticized starch/5% tunicin whiskers | 142.6 | | |
| 90% Plasticized starch/10% tunicin whiskers | 149.2 | | |
| 85% Plasticized starch/15% tunicin whiskers | 139 | | |
| 75% Plasticized starch/25% tunicin whiskers | 143.2 | | |
| 100% Plasticized starch/0% tunicin whiskers | 142.8 | 58% RH | |
| 95% Plasticized starch/5% tunicin whiskers | 140.0 | | |

(*Continued*)

**TABLE 2-4**   *Continued*

| Components | $T_m$ (°C) | Conditions | References |
|---|---|---|---|
| 90% Plasticized starch/10% tunicin whiskers | 141.4 | | |
| 85% Plasticized starch/15% tunicin whiskers | 137.6 | | |
| 75% Plasticized starch/25% tunicin whiskers | 138.1 | | |
| 100% Plasticized starch/0% tunicin whiskers | 123.1 | 98% RH | |
| 95% Plasticized starch/5% tunicin whiskers | 124.8 | | |
| 90% Plasticized starch/10% tunicin whiskers | 135.6 | | |
| 85% Plasticized starch/15% tunicin whiskers | 126.3 | | |
| 75% Plasticized starch/25% tunicin whiskers | 130.1 | | |
| Cellulose propionate difluoroethoxy acetate | 218 | – | Glasser et al. (2000) |

Mathew and Dufresne (2002) examined the thermal properties of sorbitol-plasticized starch conditioned at 0% up to 98% RH. It was observed that $T_g$ was decreased with moisture content. Furthermore, an increase of $T_m$ was observed when the RH increased from 43% to 58%. For higher moisture content (up to 75% RH), $T_m$ tended to stabilize. For the more moist sample (98% RH), an effective plasticization was reported because $T_m$ decreased (see Table 2-4).

According to Arvanitoyannis and Biliaderis (1999), at total plasticizer content (water, glycerol, and sugars) higher than 15%, a substantial depression of the $T_g$ was observed. Glycerol had a greater depressive effect on $T_g$ than sorbitol.

For glycerol-plasticized starch/tunicin whiskers composite films, the higher moisture content, the higher the melting temperature (at 75% RH the $T_m$ was about 215°C) (Table 2-4) (Anglés and Dufresne, 2001). The $T_g$ values of starch–cellulose blends are presented in Table 2-3.

### 2.4.3   Water Vapor Transmission Rate and Gas Permeability

The gas permeability (GP) measurements of plasticized starch/MC blends showed increases in GP proportional to the plasticizer content due to weakening of the intermolecular forces between adjacent polymeric chains, which facilitates chain mobility and redistribution of the originally existing voids (Arvanitoyannis, 1999). Furthermore, the GP of the soluble starch/MC blends increased proportionally to the total plasticizer content (water, glycerol, and sugars) (Arvanitoyannis and Biliaderis, 1999).

**TABLE 2-5  Water Vapor Transmission Rate (WVTR) and Gas Permeability (GP) of Various Starch–Cellulose Blends**

| Components | WVTR (g m$^{-1}$ s$^{-1}$ Pa$^{-1}$) $\times 10^{-11}$ | GP$_{O_2}$ (cm$^2$ s$^{-1}$ Pa$^{-1}$) | GP$_{N_2}$ (cm$^2$ s$^{-1}$ Pa$^{-1}$) | GP$_{CO_2}$ (cm$^2$ s$^{-1}$ Pa$^{-1}$) | References |
|---|---|---|---|---|---|
| 45% Corn starch/45% methyl cellulose/5% glycerol/5% water | 3.2 | $9.8 \times 10^{-15}$ | $6.0 \times 10^{-16}$ | $8.5 \times 10^{-14}$ | Arvanitoyannis and Biliaderis (1999) |
| 40% Corn starch/40% methyl cellulose/15% glycerol/5% water | 6.5 | $6.5 \times 10^{-14}$ | $5.3 \times 10^{-15}$ | $3.6 \times 10^{-13}$ | |
| 32.5% Corn starch/32.5% methyl cellulose/30% glycerol/5% water | 20.7 | $4.7 \times 10^{-11}$ | $2.0 \times 10^{-12}$ | $4.2 \times 10^{-10}$ | |
| 45% Corn starch/45% methyl cellulose/5% sorbitol/5% water | 4.5 | $3.4 \times 10^{-14}$ | $6.9 \times 10^{-15}$ | $7.6 \times 10^{-13}$ | |
| 40% Corn starch/40% methyl cellulose/15% sorbitol/5% water | 7.9 | $8.8 \times 10^{-14}$ | $3.6 \times 10^{-14}$ | $5.4 \times 10^{-12}$ | |
| 32.5% Corn starch/32.5% methyl cellulose/30% sorbitol/5% water | 26.5 | $5.7 \times 10^{-11}$ | $4.3 \times 10^{-12}$ | $9.0 \times 10^{-10}$ | |
| 45% Corn starch/45% methyl cellulose/5% xylose/5% water | 4.9 | $1.5 \times 10^{-14}$ | $5.7 \times 10^{-15}$ | $2.1 \times 10^{-14}$ | |
| 40% Corn starch/40% methyl cellulose/15% xylose/5% water | 8.6 | $9.9 \times 10^{-14}$ | $9.1 \times 10^{-15}$ | $8.5 \times 10^{-13}$ | |
| 32.5% Corn starch/32.5% methyl cellulose/30% xylose/5% water | 28.7 | $6.5 \times 10^{-11}$ | $4.9 \times 10^{-12}$ | $7.0 \times 10^{-10}$ | |
| 45% Corn starch/45% methyl cellulose/0% glycerol/10% water | 0.65 | $5.1 \times 10^{-14}$ | $3.9 \times 10^{-15}$ | $2.1 \times 10^{-13}$ | |
| 42.5% Corn starch/42.5% methyl cellulose/5% glycerol/10% water | 7.2 | $8.0 \times 10^{-14}$ | $9.5 \times 10^{-14}$ | $8.4 \times 10^{-13}$ | |
| 37.5% Corn starch/37.5% methyl cellulose/15% glycerol/10% water | 9.6 | $4.7 \times 10^{-13}$ | $2.5 \times 10^{-13}$ | $3.8 \times 10^{-12}$ | |

*(Continued)*

**TABLE 2-5** *Continued*

| Components | WVTR (g m$^{-1}$ s$^{-1}$ Pa$^{-1}$) × 10$^{-11}$ | GP$_{O_2}$ (cm$^2$ s$^{-1}$ Pa$^{-1}$) | GP$_{N_2}$ (cm$^2$ s$^{-1}$ Pa$^{-1}$) | GP$_{CO_2}$ (cm$^2$ s$^{-1}$ Pa$^{-1}$) | References |
|---|---|---|---|---|---|
| 30% Corn starch/30% methyl cellulose/30% glycerol/10% water | 25.9 | $3.0 \times 10^{-10}$ | $4.3 \times 10^{-13}$ | $3.2 \times 10^{-9}$ | |
| 42.5% Corn starch/42.5% methyl cellulose/5% sorbitol/10% water | 9.5 | $2.4 \times 10^{-13}$ | $8.6 \times 10^{-14}$ | $3.8 \times 10^{-12}$ | |
| 37.5% Corn starch/37.5% methyl cellulose/15% sorbitol/10% water | 14.9 | $8.7 \times 10^{-13}$ | $4.5 \times 10^{-13}$ | $2.5 \times 10^{-11}$ | |
| 30% Corn starch/30% methyl cellulose/30% sorbitol/10% water | 33.5 | $6.0 \times 10^{-10}$ | $6.3 \times 10^{-11}$ | $4.3 \times 10^{-9}$ | |
| 42.5% Corn starch/42.5% methyl cellulose/5% xylose/10% water | 8.3 | $3.8 \times 10^{-13}$ | $7.0 \times 10^{-14}$ | $8.5 \times 10^{-13}$ | |
| 37.5% Corn starch/37.5% methyl cellulose/15% xylose/10% water | 13.8 | $8.3 \times 10^{-13}$ | $4.9 \times 10^{-13}$ | $4.9 \times 10^{-12}$ | |
| 30% Corn starch/30% methyl cellulose/30% xylose/10% water | 29.6 | $7.5 \times 10^{-10}$ | $4.0 \times 10^{-11}$ | $4.0 \times 10^{-10}$ | |
| 47.5% Corn starch/47.5% MCC/0% glycerol/5% water | 0.2 | $1.8 \times 10^{-17}$ | $3.2 \times 10^{-18}$ | $1.2 \times 10^{-16}$ | Psomiadou et al. (1996) |
| 42.5% Corn starch/42.5% MCC/10% glycerol/5% water | 3.4 | $3.6 \times 10^{-15}$ | $6.5 \times 10^{-16}$ | $3.1 \times 10^{-14}$ | |
| 34% Corn starch/34% MCC/27% glycerol/5% water | 11.4 | $3.0 \times 10^{-13}$ | $3.7 \times 10^{-14}$ | $0.7 \times 10^{-12}$ | |
| 45% Corn starch/45% MCC/5% sorbitol/5% water | 2.5 | $4.0 \times 10^{-16}$ | $4.3 \times 10^{-17}$ | $2.5 \times 10^{-15}$ | |
| 39.5% Corn starch/39.5% MCC/16% sorbitol/5% water | 7.0 | $3.7 \times 10^{-15}$ | $2.8 \times 10^{-16}$ | $1.3 \times 10^{-14}$ | |
| 33.5% Corn starch/33.5% MCC/28% sorbitol/5% water | 14.2 | $4.5 \times 10^{-12}$ | $0.7 \times 10^{-13}$ | $1.5 \times 10^{-11}$ | |

| | | | | |
|---|---|---|---|---|
| 44.5% Corn starch/44.5% MCC/ 6% sucrose/5% water | 3.8 | $1.5 \times 10^{-16}$ | $0.9 \times 10^{-17}$ | $1.4 \times 10^{-15}$ |
| 40% Corn starch/40% MCC/ 15% sucrose/5% water | 8.4 | $1.1 \times 10^{-15}$ | $0.8 \times 10^{-16}$ | $1.1 \times 10^{-14}$ |
| 34.5% Corn starch/34.5% MCC/ 26% sucrose/5% water | 16.3 | $3.0 \times 10^{-12}$ | $0.7 \times 10^{-13}$ | $1.9 \times 10^{-11}$ |
| 45% Corn starch/45% MCC/ 5% xylose/5% water | 2.8 | $1.6 \times 10^{-16}$ | $1.1 \times 10^{-17}$ | $1.0 \times 10^{-15}$ |
| 39.5% Corn starch/39.5% MCC/ 16% xylose/5% water | 7.4 | $1.5 \times 10^{-15}$ | $0.9 \times 10^{-16}$ | $1.2 \times 10^{-14}$ |
| 35% Corn starch/35% MCC/ 25% xylose/5% water | 13.6 | $3.0 \times 10^{-13}$ | $5.5 \times 10^{-14}$ | $2.9 \times 10^{-12}$ |
| 47.5% Corn starch/47.5% methyl cellulose/0% glycerol/5% water | – | $2.2 \times 10^{-17}$ | $1.8 \times 10^{-17}$ | $2.0 \times 10^{-16}$ |
| 42.5% Corn starch/42.5% methyl cellulose/10% glycerol/5% water | – | $4.5 \times 10^{-15}$ | $1.8 \times 10^{-17}$ | $4.7 \times 10^{-14}$ |
| 34% Corn starch/34% MCC/ 27% glycerol/5% water | – | $4.9 \times 10^{-13}$ | $1.8 \times 10^{-17}$ | $1.5 \times 10^{-12}$ |
| 45% Corn starch/45% methyl cellulose/ 5% sorbitol/5% water | – | $6.1 \times 10^{-16}$ | $1.8 \times 10^{-17}$ | $3.8 \times 10^{-15}$ |
| 39.5% Corn starch/39.5% methyl cellulose/16% sorbitol/5% water | – | $6.5 \times 10^{-15}$ | $1.8 \times 10^{-17}$ | $2.6 \times 10^{-14}$ |
| 33.5% Corn starch/33.5% methyl cellulose/28% sorbitol/5% water | – | $6.4 \times 10^{-12}$ | $1.8 \times 10^{-17}$ | $2.8 \times 10^{-11}$ |
| 44.5% Corn starch/44.5% methyl cellulose/6% sucrose/5% water | – | $2.8 \times 10^{-16}$ | $1.8 \times 10^{-17}$ | $1.7 \times 10^{-15}$ |
| 40% Corn starch/40% methyl cellulose/ 15% sucrose/5% water | – | $2.0 \times 10^{-15}$ | $1.8 \times 10^{-17}$ | $2.2 \times 10^{-14}$ |
| 34.5% Corn starch/34.5% methyl cellulose/26% sucrose/5% water | – | $5.1 \times 10^{-13}$ | $1.8 \times 10^{-17}$ | $4.5 \times 10^{-12}$ |

Psomiadou et al. (1996) revealed that the higher the starch content in edible fibers made from MCC, MC and corn starch and polyols, the higher the water vapor transmission rate (WVTR). In addition, the high MCC/starch or MC/starch contents in the blend decreased the GP of the blend, whereas the incorporation of high water or polyol contents resulted in substantial enhancement of GP values.

WVTR and GP values of various starch–cellulose blends are presented in Table 2-5.

## 2.5   APPLICATIONS

Depending on the degree of substitution (DS) of the free hydroxyl groups, starch acetate may be used in a number of commercially important ways. Low-DS acetates are important in food applications while highly derivatized starches with a DS of 2–3 are useful because of their solubility in organic solvents and ability to form films and fibers (URL6).

Chemically modified starches have a wide spectrum of applications, but the most important areas are in the paper, food and textile industries. Hydroxyethyl starch is used extensively in paper manufacturing, in the pharmaceutical industry as a plasma volume extender, and as adhesives. Hydroxypropyl-modified starches are of great importance in food and food-related products, primarily as thickeners, and as excipients in foods and pharmaceuticals. Cationic starches are used in large quantities in paper manufacturing. Cationic ethers with tertiary aminoalkyl groups or with quaternary ammonium groups are used in hair care products and as bactericides (Richardson and Gorton, 2003; URL2).

Cellulose acetate of certain degrees of acetylation is commonly used to manufacture cigarette tow, textile fibers, films, plastics, and other materials (URL6). Cellulose acetate is also used for wrapping baked goods and fresh produce. Although cellulose acetate requires the addition of plasticizers for production of films, the resulting product demonstrates good gloss and clarity, good printability, rigidity, and dimensional stability. Although these films can tear easily, they are tough and resistant to punctures (Liu, 2006).

Carboxymethyl cellulose (CMC) is used in coatings, detergents, food, toothpaste, adhesives, and cosmetics applications. Hydroxyethyl cellulose and its derivatives are used as thickeners in coatings and drilling fluids. Methyl cellulose is used in foods, adhesives, and cosmetics. Cellulose acetate is employed in packaging, fabrics, and pressure-sensitive tapes (URL1).

The major markets for CMC are in detergents, in textiles and in paper manufacturing. Another cellulose ether much used in industry is hydroxyethyl cellulose (HEC). This product acts, for example, as a thickener in drilling fluids, as a moisture-retaining agent and retarder in cements, and as a thickener in the oil industry and a suspension aid in paints. Ethyl(hydroxyethyl) cellulose (EHEC) is a mixed ether that is widely used in the paint and building industries; in the former as protective colloids, thickeners, and pigment suspension aids, and in the latter as dispersion agents in cement formulations (Richardson and Gorton, 2003). Cellulose ethers, such as methylcellulose, are widely used as gelling and dispersing agents in foods, cosmetics,

**TABLE 2-6    Applications of Cellulose and Starch Derivatives and Starch–Cellulose Blends**

| Components | Applications | References |
|---|---|---|
| Starch acetate | Food applications, films, fibers | URL6 |
| 2-Hydroxyethyl starch | Paper industry, textiles, films, plasma extenders | Richardson and Gorton (2003); URL2 |
| 2-Hydroxypropyl starch | Food products, films, excipients in foods and pharmaceuticals | |
| Cationic starches | Paper industry, textiles, hair care products, bactericides | |
| Succinate starch | Films, emulsions | Richardson and Gorton (2003) |
| Acetyl starch | Food products, textiles, paper industry | Richardson and Gorton (2003) |
| Crosslinked starch | Food products, emulsions | Richardson and Gorton (2003) |
| Anionic starches | Paper, adhesives | Richardson and Gorton (2003) |
| Cellulose acetate | Cigarette tow, textile fibers, films, plastics, wrapping goods, packaging, fabrics, pressure-sensitive tapes | URL6; Liu (2006) |
| Ethyl cellulose | Paints, lacquers | Richardson and Gorton (2003) |
| 2-Hydroxyethyl cellulose | Paints, emulsions, drilling mud | Richardson and Gorton (2003) |
| 2-Hydroxypropyl cellulose | Building materials, paints, tablets | Richardson and Gorton (2003) |
| Sodium carboxymethyl cellulose | Detergents, textiles, food products | Richardson and Gorton (2003) |
| Methyl cellulose | Foods, adhesives, cosmetics, building materials, paint removers, gelling and dispersing agents in foods, cosmetics, pharmaceuticals and lacs | URL2 |
| Ethyl cellulose | Carriers for the controlled release of nitrogen fertilizers | URL2 |
| Hydroxypropyl cellulose | Coating of paper and tablets | URL2 |
| Hydroxypropyl methyl cellulose | Agent for lowering blood cholesterol levels | URL2 |
| Cellulose acetate propionate or butyrate | Toys, sport goods, ophthalmic and medical applications | URL2 |
| Cellulose acetate phthalate | Tablet production | URL2 |
| Carboxymethyl cellulose | Coatings, detergents, food, toothpaste, adhesives, cosmetics applications | URL1 |
| Hydroxyethyl cellulose and derivatives | Thickeners in coatings and drilling fluids | URL1 |

*(Continued)*

**TABLE 2-6**    *Continued*

| Components | Applications | References |
|---|---|---|
| 50–99% Cellulose acetate/ 1–50% starch acetate blend | Fibers, filaments, yarns, fabrics, plastic materials | URL6 |
| Oxidized starch and cellulose imine derivatives | Antimalarial activity | Taba Ohara et al. (1995) |
| 70% Rice starch/30% microcrystalline cellulose | Compressible excipient | Limwong et al. (2004) |

pharmaceuticals, and lacs. Ethyl cellulose has been evaluated for carriers for the controlled release of nitrogen fertilizers. Hydroxypropyl cellulose (HPC) has excellent surface and film-forming properties and is thus used for coating of paper and tablets. Hydroxypropylmethyl cellulose (HPMC) is a promising agent for lowering blood cholesterol levels. Cellulose acetate propionate (CAP) or butyrate (CAB) are used to make toys, sport goods, and in ophthalmic and medical applications. Cellulose acetate phthalate is used for tablet production (URL2).

A blend of 50–99% cellulose acetate with 1–50% starch acetate offers the possibility of combining a cheap raw material, starch, with the production of fibers, filaments, yarns, fabrics, plastic materials, and other uses (URL6).

Oxidized starch imine derivatives of sulfonamides or pyrimidine—derivatives of sulfisoxazole (ML8), sulfameter (ML11) and trimethoprim (ML13)—and oxidized cellulose imine derivatives of dapsone (ML14), sulfadiazine (ML17), sulfamethoxazole (ML18), sulfisoxazole (ML19), sulfamethoxypyridazine (ML20) and sulfameter (ML22) were submitted to in-vivo biological assays with mice infected with *Plasmodium berghei*. Only ML11 was 100% curative, while ML17 showed the same effect as its prototype (Taba Ohara et al., 1995).

Rice starch (RS) and microcrystalline cellulose in the ratio 7 : 3 was proposed as a suitable combination with respect to its properties for use as a new co-processed directly compressible excipient. The tablets made from these co-processed composite particles exhibited high compressibility, good flowability, and self-disintegration (Limwong et al., 2004).

Various applications of cellulose and starch derivatives, and starch–cellulose blends are presented in Table 2-6.

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■■■■ **CHAPTER 3**

# Starch–Sodium Caseinate Blends

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## 3.1   INTRODUCTION

The continuously increasing interest of consumers in quality, convenience, and food safety has encouraged further research into edible films and coatings (Krochta et al., 1994; Herald et al., 1995). The reinvention of "edible films" was due mainly to their numerous applications such as coatings for sausages, fruits and vegetables, chocolate coatings for nuts, and occasionally wax coatings (Camirand et al., 1992; Park et al., 1994). Although the use of edible films has multiple objectives, among the most important may be considered restriction of moisture loss, control of gas permeability,

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control of microbial activity (e.g., chitin has an antimicrobial action), preservation of the structural integrity of the product, and gradual release of enrobed flavors and anti-oxidants in food (El Ghaouth et al., 1991; Wong et al., 1992). Edible films are primarily composed of polysaccharides, proteins and lipids, alone or in combination. Such films should possess suitable gas and aroma barrier and mechanical properties, to protect foodstuffs from deterioration. Combining polysaccharides and proteins in the form of blends or layers, with varying ratios of polymers, offers the possibility of creating different films with improved characteristics (Kristo et al., 2007).

Starch constitutes more than 60% of cereal kernels and is relatively easy to separate from the other chemical components. The other components, such as fibers, protein and fat, have a market value of their own as food or feed (Rexen et al., 1988). Starch (starch : water 30% w/w) was rendered amorphous by gelatinizing and roller drying (in one process) at 140°C, pressure 32 psi (221 kPa), and width 150 mm (Arvanitoyannis et al., 1996). Apart from some high-amylose and modified starches (crosslinked, methylated), starch in general does not form tough, pliable, and unsupported films. Nevertheless, it has found extensive use in the formulation of adhesives and sizings to improve the mechanical properties of items such as paper and textiles, in which the film-forming ability is of great importance (Young, 1984). Starch is the polysaccharide most commonly used to produce the protein–polysaccharide gels used in the food industry. In the dairy industry, the use of starch in the formulation of some dairy products has improved their texture and viscosity and promoted significant cost savings. Interactions between starch and milk proteins are anticipated to greatly affect the rheological properties of food systems (Lelievre and Husbands, 2002), markedly changing the gel network structure and the rheological profile (Goel et al., 1999).

Casein and casein derivatives have found many applications in the food and pharmaceutical industries (Southward, 1989). The unique characteristics of milk proteins make them excellent candidates for incorporation into edible films and coatings to control mass transfer in food systems (Avena-Bustillos and Krochta, 1993). Sodium caseinate was selected for these experiments because it is commercially available, has satisfactory thermal stability, and can easily form films from aqueous solutions due to its random coil nature and its ability to form extensive intermolecular hydrogen bonds, electrostatic bonds, and hydrophobic bonds (Arvanitoyannis and Biliaderis, 1998). The physical properties of edible films based on blends of sodium caseinate with starches of different origin (corn and wheat) plasticized with water, glycerol, or sugars were also reported by Arvanitoyannis et al. (1996). Casein and casein derivatives vary in molecular weight (19,000–23,900) and have been used extensively in the food industry (dairy, meat, and confectionery) and in medical and pharmaceutical applications (URL1). Sodium caseinate readily forms films, owing to its high water solubility, its random-coil structure, and its capacity to form chain aggregates via electrostatic forces, van der Waal's forces, and hydrophobic interactions (McHugh and Krochta, 1994). Despite the fact that starch and casein are involved in many food formulations, very few studies have focused on their interactions. The understanding of caseinate–starch interactions is an important tool that could be used to manipulate

the rheological properties of food systems and to provide alternatives in the development of new products (Bertolini et al., 2005).

## 3.2  STARCH AND STARCH DERIVATIVES

Starch is mostly water soluble, difficult to process, and brittle when used without the addition of a plasticizer. Furthermore, its mechanical properties are very sensitive to moisture content, which is difficult to control. In principle, some properties of starch can be significantly improved by blending it with synthetic polymers (Dufresne et al., 2000). Starch alone cannot form films with satisfactory mechanical properties (high percentage elongation and tensile and flexural strength) unless it is plasticized, blended with other materials, chemically modified, or modified with a combination of these treatments (Liu, 2006).

Starch derivatives include dextrins, starch esters, and starch ethers. The starch esters most commonly used are esters with phosphoric acid (phosphate starches) and acetic acid (acetyl starches). The three most important starch ethers are the hydroxyethyl, hydroxypropyl, and carboxymethyl starches. Starch derivatives based on esters can be biologically reduced, while starches based on ethers are more difficult to biodegrade. However, the great variety of possible chemical modifications makes it possible to produce good slashing agents, which can be virtually completely biodegraded (URL2).

Starch is a highly hydrophilic material that contains anhydroglucose units linked by $\alpha$-D-1,4-glycosidic bonds. The water absorbed by starch granules is mainly bound in the amorphous phase. At certain temperatures, shear stress, and pressure in an extruder, the gelatinization processing disrupts the crystalline and ordered structure in starch granules to produce an amorphous phase (Yu et al., 2007). Starch granules vary in size from about 2 to 150 mm (Kerr, 1950). Pure starch, as distinct from commercial starch, is a white, odorless, tasteless, neutral powder, insoluble in cold water or organic solvents (Radley, 1953). Most starch granules are composed of a mixture of two polymers (Ahmad et al., 1999), namely, amylose and amylopectin. The amylose content can vary over a broad range, from 0% to about 75%, but typically is 20–25% (w/w) (Parker and Ring, 1996). In addition, starch is easily hydrolyzed to fermentable substrates (Rexen et al., 1988).

### 3.2.1  Mechanical Properties

Dufresne et al. (2000) examined the mechanical behavior of an unfilled starch–glycerol matrix at room temperature as a function of glycerol content and relative humidity (RH). With increasing glycerol content, a decrease in the modulus was observed regardless of RH. This decrease was linear up to ∼15% glycerol. At a higher glycerol content, the drop in modulus drop increased strongly.

The tensile modulus of unfilled starch–glycerol matrix films ranged between 0.24 and 20 MPa, depending greatly on the water content. The 35% RH conditioned sample displayed a typical rubberlike behavior with a high strain at break

($\sim$140%). As the water content increased, starch tended to crystallize, and the elongation at break decreased strongly (up to 18% at 43% RH). No significant difference was reported for more moist specimens. The strength of the material was almost moisture independent and ranged between 0.25 and 1 MPa (Anglés and Dufresne, 2001).

Avérous and Boquillon (2004) investigated the thermal and mechanical behavior of two different plasticized starch matrixes [TPS$_1$: dried wheat starch (70 wt%), glycerol (18 wt%) and water (12 wt%); TPS$_2$: dried wheat starch (65 wt%) and glycerol (35 wt%)]. The elongation at break was 124% for TPS$_1$ and 60% for TPS$_2$. The maximum tensile stress was 3.6 MPa and 1.4 MPa for TPS$_1$ and TPS$_2$, respectively, while the tensile modulus was 87 MPa for TPS$_1$ and 12 MPa for TPS$_2$. It can be concluded that the less plasticized matrix shows higher mechanical behavior. Avérous et al. (2001b) reported that the plasticized wheat starch (PWS) tensile modulus and strength was 52 and 3 MPa, respectively, while the elongation at break was 126%. According to Avérous et al. (2001a), the tensile strength and modulus of TPS was 3.6 MPa and 87 MPa, respectively, and the elongation at break was 124%.

Starch acetate was blended with corn stalk fibers at different concentrations (0%, 2%, 6%, 10%, and 14% w/w) for the production of biodegradable extruded foams. The force required for shearing the extrudates increased with an increase in fiber content from 1% to 10%. There was a drastic increase in the force (0.06–0.075 N/mm$^2$) required to shear the extrudates with 14% fiber content (Ganjyal et al., 2004).

### 3.2.2  Thermal Properties

Native starch (NS) was extracted from natural corn grain or from alkaline temperature-treated corn (95°C/40 min in a 10% lime solution) (ATS). The NS and the ATS starches were stored (30°C) at different relative humidities (%RH) (11–84%) (URL3). In the experiment conducted by Avérous and Boquillon (2004), the glass transition temperature ($T_g$) (by differential scanning calorimetry [DSC] analysis) was 87°C for TPS$_1$ and 12°C for TPS$_2$. On the other hand, Avérous and Fringant (2001) found that the $T_g$ values of various TPS formulations were below ambient temperature except for the 74% starch/10% glycerol/16% water blend.

The $T_g$ and melting temperature ($T_m$) (by DSC) of the starches were determined at different storage times. The $T_g$ of the starches in 80% water dispersion was between 60°C and 65°C. However, after the thermal treatment, $T_g$ was increased ($-14$°C to 0°C) (URL3).

### 3.3  SODIUM CASEINATE DERIVATIVES

The effect of sodium caseinate (NaCas) on the rheological properties of starch pastes has also been studied (Kelly et al., 1995). Although NaCas was found to decrease the viscosity of potato starch, its addition to maize starch resulted in an increase in viscosity. These studies showed that, in distilled deionized water, NaCas increased the swelling properties of the starch granules. More recently, Bertolini et al. (2005)

studied the rheological properties of NaCas–starch gels. They reported that, when added to cassava, amylomais corn, waxy corn, wheat, or rice starch, NaCas increased the elastic modulus and the viscosity of the gel compared with the gel made using starch alone. However, when added to potato starch, NaCas decreased the viscosity of the NaCas/potato starch mixture. In the case of potato starch, although no clear explanation for the decrease in viscosity was proposed, the authors suggested that the role of minerals, such as phosphorus, calcium, and sodium, might be important and thus should be investigated (Noisuwan et al., 2008).

Caseinate films exhibit resistance to thermal denaturation and/or coagulation, which means that the protein film remains stable over a wide range of pH, temperature, and salt concentration (Kinsella, 1984). The structural and shear characteristics of mixed monolayers formed by an adsorbed NaCas film and a spread monoglyceride (monopalmitin or monoolein) on a previously adsorbed protein film have been analyzed. Measurements of the surface pressure ($\pi$)–area ($A$) isotherm and surface shear viscosity were obtained at 20°C and at pH 7 in a modified Wilhelmy-type film balance. The structural and shear characteristics depend on the surface pressure and on the composition of the mixed film. At surface pressures lower than the equilibrium surface pressure of NaCas, both NaCas and monoglyceride coexist at the interface, with structural polymorphism or a liquid expanded structure due to the presence of monopalmitin or monoolein in the mixture, respectively. At higher surface pressures, collapsed NaCas residues may be displaced from the interface by monoglyceride molecules. For a NaCas–monopalmitin mixed film, the $\eta_s$ value varies greatly with the surface pressure (or surface density) of the mixed monolayer at the interface. In general, the greater the surface pressure, the greater are the values of $\eta_s$. However, the values of $\eta_s$ for a NaCas–monoolein mixed monolayer are very low and practically independent of the surface pressure (Rodriguez Patino et al., 2007) (see Table 3-1).

### 3.3.1  Mechanical Properties

The maximum load (ML) and tensile strength (TS) of NaCas films decreased linearly with increasing glycerol. Films with no glycerol were found to be the strongest with a mean TS value of 37 MPa. Elongation (%E) increased with increasing glycerol content. The load–displacement curve for films manufactured without plasticizer showed an inverted "V" shape, i.e., a sharp increase in load followed by a sharp decrease after reaching the ML value. These films were only slightly extensible and shattered into small pieces at the end of the test. In contrast, films containing glycerol were better able to withstand the gradual increase in extension during the elongation test. The standard deviation for the determination of %E increased with increasing glycerol content. Increasing the glycerol content did not have a significant effect on the water vapor permeability (WVP) of the films, with the exception of the films with Gly : Pro ratio of 0.32. The latter had a significantly higher WVP than films with Gly : Pro ratio of 0.16 or less (Shou et al., 2005).

Tensile strength (TS) and percentage elongation at break (%E) were measured at $20 \pm 1$°C with an Instron universal testing instrument according to AFNOR standard

**TABLE 3-1   Sodium Caseinate Analysis**

| Analyses | | References |
|---|---|---|
| *Typical Analysis* | | |
| Protein (dry basis): Nx6.38 | 91.0% | URL4 |
| Moisture | 6.0% | |
| Fat | 2.5% | |
| Ash | 5.0% | |
| Carbohydrate | 1.0% | |
| pH | 6.6–7.2 | |
| *Typical Microbiological Analysis* | | |
| Standard plate count | $<20,000/g$ | URL4 |
| Coliform | $<10/g$ | |
| *Escherichia coli* | Negative | |
| Yeast/mold | $<100/g$ | |
| *Salmonella* | Negative | |
| *S. aureus* | Negative | |
| *Typical Amino Acid Content* (g/100 g of protein) | | |
| Alanine | 2.6 | URL5 |
| Arginine | 3.6 | |
| Aspartic acid | 6.3 | |
| Cystine | 0.3 | |
| Glutamic acid | 20.0 | |
| Glycine | 2.4 | |
| Histidine | 2.7 | |
| Isoleucine | 5.4 | |
| Leucine | 8.2 | |
| Lysine | 7.3 | |
| Methionine | 2.5 | |
| Phenylalanine | 4.4 | |
| Proline | 10.1 | |
| Serine | 5.6 | |
| Threonine | 4.3 | |
| Tryptophan | 1.1 | |
| Tyrosine | 5.6 | |
| Valine | 6.4 | |

method NF T 54-102 (AFNOR, 1971). Five specimens were cut from each preconditioned film (50% RH, 20°C) and uniaxially stretched at a constant rate of 100 mm/min until breaking. Tests were carried out over a period of about 10 min to minimize exposure of the samples to the ambient environment.

The general trend of the stress–strain curve of triethanolamine (TEA)-plasticized samples crosslinked by 1% formaldehyde is similar to the shape of that for the noncrosslinked samples. For TEA-plasticized films crosslinked with 2–10% w/w

formaldehyde (HCHO/ε-NH$_2$ = 1.35–6.75; ε-NH$_2$ = free amino groups), the stresses at break, about 8–9 MPa, were more than twice the values of TEA/NaCas films without formaldehyde and ultimate strain values were up to 110–125%. Compared with only plasticized samples, small amounts (1% w/w; HCHO/ε-NH$_2$ = 0.67) of HCHO did not initiate major changes in elastic modulus (about 46 MPa in both cases). For HCHO/ε-NH$_2$ ratios ranging from 1.35–6.75, the Young's modulus increased to about 100–110 MPa, which is more than twice the value of TEA/NaCas films without HCHO. The mechanical properties of crosslinked plasticized NaCas films increased with the concentration of crosslinking agent. An HCHO/ε-NH$_2$ ratio of 1.35 seemed to be optimal for enhancing mechanical properties of plasticized caseinate films. Although the mechanical properties dependent on the ratio of crosslinker to protein in a limited range, further crosslinking does not seem to affect the film performance from a mechanical point of view (Audic and Chaufer, 2005).

## 3.3.2 Thermal Properties

Differential scanning calorimetry (DSC) measurements of the starch samples were performed with a Pyris-1 Thermal Analytical System (Perkin-Elmer, Norwalk, CT, USA). Samples were weighed in steel pans and distilled water or NaCas solution was added (10 mg of starch, dry basis, to 20 μL of water or NaCas solution) before sealing. The sealed pans were equilibrated overnight at 4°C and then heated from 25 to 180°C at a heating rate of 3°C/min. Indium was used for calibration, and an empty pan was used as a reference. Enthalpy changes ($\Delta H$), the gelatinization onset temperature ($T_{onset}$), the gelatinization range ($T_2 - T_1$), and the peak temperature ($T_{peak}$) were calculated automatically. Statistical analyses of RVA (rapid visco analyzer) and DSC data were assessed considering starch, NaCas, and their interactions. The RVA data were analyzed for peak viscosity, final viscosity, and peak temperature. The DSC data were analyzed for enthalpy, temperature of gelatinization, peak temperature, peak start temperature, and peak end temperature (Bertolini et al., 2005).

Pullulan, NaCas, and their mixtures in different ratios were dissolved in distilled water under continuous stirring, to obtain casting solutions of 4% (w/w) concentration. Sorbitol at a concentration of 25% dry basis (db), was added as a plasticizer to the polymer solutions and this concentration was kept constant throughout the study. Such a concentration of sorbitol was necessary because films containing NaCas were very difficult to handle without breaking when lower plasticizer levels were used. The solutions were subsequently filtered to remove any undissolved material and vacuum degassed to remove air bubbles, and 20 g samples of the solution was cast on plastic frames. The frames were then stored in an oven at 35°C, allowing them to dry slowly (Kristo et al., 2007).

The glass transition determination was also carried out with DSC; the $T_g$ was determined as the middle temperature of the observed change in heat capacity from the second DSC scan to eliminate the effects of sample history (Kalichevsky and Blanshard, 1993). However, in some cases, it was difficult to determine the $T_g$ accurately from the DSC scans, particularly for samples containing NaCas, because with

this material the $T_g$ value was often smeared out over a broad temperature range. Also, when low temperatures were involved, in some cases it was impossible to determine the $T_g$ values (e.g., because of ice interference). These difficulties, mainly related to proteins and foodstuffs, are often reported in the literature (Le Meste et al., 1996).

## 3.4   STARCH–SODIUM CASEINATE BLENDS

Protein-based films were cast from film-forming solutions of wheat gluten, corn zein, egg albumin, and NaCas (Rhim et al., 1999). Edible films based on soluble starch/NaCas blends, plasticized with water and/or other polyols, were studied with regard to their thermal, mechanical, and gas and water vapor barrier properties. Macroscopically examined, the films appeared to be clear, suggesting a homogeneous distribution of the two or three components in the blend. At a total plasticizer content lower than 17%, both thermal and mechanical properties of the blends remained within acceptable limits for packaging or coating applications. A marked change was observed in the mechanical properties at higher than 17% total plasticizer content, possibly due to a disruption, at least in part, of the soluble starch/NaCas amorphous matrix (Arvanitoyannis and Biliaderis, 1998).

The shear characteristics of pure and caseinate–monoglyceride mixed films were sensitive to the composition of the mixed film and to the surface pressure. This is due to lateral interactions between the proteins due to hydrogen bonding, hydrophobic and covalent bonding, and/or electrostatic interactions (Rodriguez Patino and Carrera, 2004). These interactions between adsorbed protein molecules may vary strongly. Moreover, for a fully packed adsorbed layer (at higher surface pressures), the deformability (i.e., the mechanical properties) of the protein molecules may be an important factor (Gunning et al., 2004). Thus, differences between $\eta_s$ values for various proteins (caseinate, β-casein, κ-casein, etc.) are quite large and reflect differences in, among other things, the protein structure and the potential for the formation of disulfide crosslinks and the formation of interfacial aggregates of significant sizes. The values of $\eta_s$ were higher for proteins that form interfacial gels by crosslinking of disulfide residues and the formation of interfacial aggregates of significant size (κ-casein and caseinate, in that order) compared with β-casein, which can only form physical gels stabilized by intermolecular hydrogen bonds (Rodriguez Patino and Carrera Sanchez, 2004). The differences in shear rheology observed between monoglyceride and caseinate monolayers justify the use of this technique to analyze the interfacial characteristics (structure, interactions, miscibility, squeezing out phenomena, etc.) of caseinate–monoglyceride mixed films at the air–water interface and thus allow a global consistency check on the same monolayer.

Caseinate exhibits thermoplastic and film-forming properties due to its random coil nature and its ability to form weak intermolecular interactions—hydrogen bonds, electrostatic bonds, and hydrophobic bonds (Creighton, 1984). These properties make sodium caseinate an interesting raw material for several applications as substitutes for traditional synthetic polymers. For their transparency, biodegradability, and good technical properties (high barrier for gases such as oxygen) (Chick and

Ustunol, 1998), caseinate-based films can find applications in packaging (Krochta et al., 1990), in edible or protective films and coatings (Chen, 1995), or in mulching films (De Graaf and Kolster, 1998). Such films are easily obtained by casting aqueous solutions of sodium caseinate. The objective has been to achieve caseinate-based films with improved properties as close as possible to those of available packaging films based on synthetic polymers such as polyethylene (Chen, 1995) or plasticized PVC (Audic et al., 2001). Such films show good elongation at break (from 150% to about 400%) and a rather low tensile strength ranging from 20 to 30 MPa. However, compared with synthetic films, protein-based films have two major drawbacks (Mauer et al., 2000; Grevellec et al., 2001): poor mechanical properties (lower tensile strength and elongation at break); and high water sensitivity (i.e., high water solubility and water vapor permeability).

Edible films were cast from solutions of sodium caseinate (NaCas) and from emulsions of this protein with anhydrous milk fat (AMF). The moisture sorption isotherms, mechanical properties (tensile strength [TS] and elongation) and water vapor and oxygen permeabilities were determined for films based on NaCas as a function of AMF concentration. AMF concentration significantly affected TS ($P < 0.001$) and elongation ($P < 0.05$). The increase of lipid content led to a loss of mechanical efficiency but had little influence on water vapor barrier properties. There was no significant difference ($P > 0.05$) between oxygen permeability of films at each lipid concentration (Khwaldia et al., 2004a).

Bilayer films were prepared by successive casting of NaCas solutions onto preformed pullulan films. For bilayer films, different polymer ratios resulted in differences in polymer layers. A mixture–process variable experimental design was employed to investigate the effect of film composition on the tensile properties of blend and bilayer films comprising pullulan and NaCas and plasticized with 25% db sorbitol. Mixture experiments are a special class of response surface experiments in which the factors are the proportions of the components and the measured property response depends on such component ratios (Kristo et al., 2007).

Plasticized protein films were prepared by the casting method from water solution of NaCas and plasticizers with the aim of obtaining environmentally friendly materials for packaging applications. Mechanical properties (tensile strength, elongation, and Young's modulus) of caseinate-based films were determined versus ratio of protein to plasticizer, plasticizer type, and relative humidity conditions. Among the different polyol-type plasticizers tested, glycerol (Gly) and triethanolamine (TEA) were the most efficient for the improvement of mechanical properties (high strains for low stresses). Further, chemical crosslinking between formaldehyde and free amino groups of sodium caseinate was done to increase water resistance of TEA-plasticized films (Audic and Chaufer, 2005).

## 3.4.1 Mechanical Properties

Edible films, from wheat and corn starch with NaCas plasticized by water or several sugars or glycerol, were tested with regard to their compatibility, mechanical strength, and gas and water vapor permeabilities. Most films, with water contents <15% w/w,

had sufficient strength and acceptable gas barrier properties and showed no phase separation. When the water/sugar content exceeded the threshold of 15% total plasticizer content, both thermal and mechanical properties showed a pronounced change because of the disruption of the starch/NaCas matrix (Arvanitoyannis et al., 1996).

It is noteworthy that similar tensile strengths were obtained for films cast from corn starch and from a solution containing 75%, by weight, amylopectin and 25%, by weight, amylose (Young, 1984). However, the mechanical properties measured by other researchers (Warburton et al., 1993) for maize grit extrudates were considerably higher (10–20 times). Such variations were explained by differences in density as well as the size and number of cavities present (Lourdin et al., 1997). Further work has to be conducted with microscopy or image analysis in order to clarify the nature of these differences.

In plasticized starches, the efficiency of plasticization with the same amount of plasticizer is dependent on the amylose/amylopectin ratio (Arvanitoyannis et al., 1996). Sorbitol has almost the same effect as glycerol on the mechanical properties of corn starch. It should be noted, however, that the increase in elongation was slightly greater than that caused by incorporation of glycerol. A possible explanation might be the higher hydroxyl number of sorbitol.

Another factor that should be borne in mind is the effect of developed crystallinity during storage of the films. It is well known from synthetic polymers that high crystallinity, in conjunction with chain orientation, has a positive influence upon the tensile strength, whereas the gas diffusion and permeation are substantially reduced (Arvanitoyannis and Blanshard, 1993; Arvanitoyannis et al., 1994). The starch-based films appeared to have adequate strength, especially when the amylopectin content was low since the branched molecules showed very limited orientation and packing ability compared to amylose (Young, 1984). Novamont tried to modify starch (within the frame of an innovatory R&D program) into a mechanically superior form devoid of crystallinity (not detectable with X-rays and dynamic thermal analysis [DTA]) and marketed several products possessing good mechanical properties (Bastioli, 1995). The upward curvature of the isotherms also suggests the formation of water clusters in the polymer matrix at high water activities. Indeed, the concomitant plasticization and swelling of the polymer matrix as the moisture content of the film increased provided more binding sites for water sorption (Lim et al., 1999). Several empirical and semiempirical equations have been proposed for the correlation of the equilibrium moisture content with the water activity of food products. Among them the Guggenheim–Anderson–de Boer (GAB) equation has been applied successfully to various foods (Van Den Berg, 1985). It is a relatively simple model with a small number of parameters that have physical meaning, and can be applied for water activities from 0 to 0.9 (Weisser, 1985).

The thermomechanical behavior of pullulan and NaCas films, either alone or with sorbitol (plasticized at 15% and 25% db level), was studied by dynamic mechanical thermal analysis (DMTA). Representative DMTA traces of plain pullulan and NaCas thick-film specimens containing or not containing sorbitol and conditioned at RH 64%. Similar behavior was observed for the samples equilibrated at other water activities. Usually the position of the tan δ peak or of the onset of $E_0$ drop is used

as definition of glass transition temperature. The rationale behind such behavior is the substantially different structures of the two polymers (Kristo and Biliaderis, 2006).

Pullulan solids mainly exist in an amorphous state due to the presence of linkages on the polysaccharide chain, which allow molecular motions to take place around the three inter-residue bonds and provide extra distance between residues (due to the third glycosidic bond); the latter lead to an apparent lack of direct inter-residue hydrogen bonding (Biliaderis et al., 1999). For the protein component (NaCas), a chain rigidification mechanism may be provided by the electrostatic interactions involving the sodium cations (Gidley et al., 1993). The addition of sorbitol drastically diminished the $T_g$ of pullulan, whereas it brought about a slight increase in $T_g$ of NaCas. Furthermore, the storage modulus of the rubbery state decreases with increasing sorbitol content in both pullulan and NaCas films.

The Gordon–Taylor (G-T) equation was applied in a purely empirical sense to describe the water content dependence of the $T_g$ of all the systems studied (Lazaridou and Biliaderis, 2002). It is obvious that the pullulan and sodium caseinate samples free of sorbitol exhibited increased sensitivity to plasticization at moisture contents below 8–10% (Gontard and Ring, 1996). Moreover, lower slopes of the G-T curves were observed when sorbitol was added, which is in agreement with the findings of Lourdin et al. (1997), who assumed a reduction of the amount of water available for efficient plasticization due to the presence of a second plasticizer.

The plasticizing effect of water was apparent in all cases, but pullulan samples exhibited greater $T_g$ depression than the NaCas films at similar sorbitol and moisture content levels. The significantly lower plasticizing effect of water on NaCas than on pullulan could probably be explained by the greater hydrophobicity of the protein (Kalichevsky et al., 1993). Even though the water uptake of both polymers was very similar (as was shown from moisture sorption isotherms), part of the water could be preferably associated with sodium ions (in NaCas), allowing an uneven water distribution within the protein structure. The addition of sorbitol brought about a notable decrease of $T_g$ for both pullulan and NaCas at low moisture content (<10% w/w). However, a different effect of sorbitol on these polymers was observed at higher water contents. Thus, the $T_g$ of the sorbitol-plasticized pullulan samples continued to decline and approached the $T_g$ of the polyol-free sample at equivalent water content, which concurs with the findings of Diab et al. (2001).

On the other hand, addition of sorbitol enhanced the $T_g$ of sodium caseinate at water contents >10% (w/w). Also, Kalichevsky et al. (1992) observed an increase in $T_g$ of gluten at higher water contents in the presence of fructose, glucose, and sucrose and attributed this behavior to an unequal distribution of water between polymer and sugar or to an increase of hydrophobic interactions in the protein structure. The last effect could arise from the ability of various sugars and polyols to stabilize proteins by increasing the structure of water, leading to intensification of hydrophobic interactions and stabilization of the protein conformation (Back et al., 1979). Kilburn et al. (2005) proposed two distinct mechanisms of polysaccharide plasticization by water and low molecular weight sugars. They assumed that water molecules form hydrogen bonds with the hydroxyl residues on the polymer chains, interrupting the polymer–polymer interactions and allowing the

polymer chains to come apart. In contrast, the plasticizing action of the low molecular weight sugars is attributed to a strong reduction in molecular entanglements upon a shift of the "apparent" molecular weight distribution to lower values.

The low-temperature transition for both plain polymers at very low water content was close to but somewhat higher than the $T_g$ of sorbitol alone, indicating probably the existence of a sorbitol-rich phase whose $T_g$ was increased by the polymer domains (Moates et al., 2001) due to an increase in the average molecular weight (Cherian et al., 1995). Similarly, Kalichevsky et al. (1992) for gluten–sugar mixtures, Kalichevsky et al. (1993) for sodium caseinate–fructose systems, and Kalichevsky and Blanshard (1993) for amylopectin–fructose samples assigned the low-temperature transition to fructose and supported the conclusion given by Kolarik (1982) that such a type of low-temperature transition is frequently observed in compatible polymer–diluent mixtures, not necessarily implying phase separation but being due to the onset of short-range motions.

The mechanical properties of various starch–NaCas blends are shown in Table 3-2.

### 3.4.2  Thermal Properties

Considering that the properties of film-forming solutions must be reflected in the behavior of the solid film, the glass transition temperature, which can be interpreted as the range of temperatures at which segment motion of macromolecules becomes thermally activated, was analyzed. The $T_g$ of proteins increases with the chain rigidity and the intensity of both inter- and intramolecular interactions, including hindrance to internal rotation along the macromolecular chain. An effective plasticizer has to shield the intermolecular and intramolecular interactions, facilitating the molecular mobility and decreasing the internal friction in the biopolymer material (Kalichevsky et al., 1993). The presence of sorbitol had a significant plasticizing effect on the NaCas film and the observation of a single glass transition reflects compatibility between sorbitol and sodium caseinate.

The interaction and, in consequence, the plasticizing effect, could be attributed to the low molecular weight of sorbitol and the presence of hydroxyl groups, leading to the formation of NaCas–sorbitol interactions, despite the polymer–polymer interactions, increasing the intermolecular spacing as a result. The six hydroxyl groups of sorbitol might interact with lateral residues of NaCas amino acids through hydrogen bonds. These interactions would decrease the partial specific volume of the protein, allowing a greater backbone chain segmental mobility of the NaCas and leading to lower values of the glass transition temperatures (Barreto et al., 2003a).

The thermal degradation of edible films based on pure NaCas, whey, and gelatin, and on these proteins in the presence of sorbitol as a plasticizer, was studied by thermogravimetry and infrared spectroscopy in nitrogen atmosphere. The presence of sorbitol significantly reduced the activation energy of the degradation of the edible protein films. This behavior was in agreement with the decrease of the initial and maximum temperatures of degradation observed by thermogravimetry. The decrease in the thermal stability is apparently associated with the effect of sorbitol on the inter- and intramolecular hydrogen bonds of the proteins. The Fourier transform infrared

**TABLE 3-2  Mechanical Properties of Starch–Sodium Caseinate Blends**

| Components | % Elongation | Tensile Strength (MPa) | Young's Modulus (MPa) | References |
|---|---|---|---|---|
| 85% Corn starch / 0% sodium caseinate / 15% water | 6.2 ± 0.4 | 38.3 ± 2.1 | 23.8 ± 2.4 | Arvanitoyannis et al. (1996) |
| 80% Corn starch / 5% sodium caseinate / 15% water | 6.9 ± 0.5 | 33.4 ± 2.2 | 24.7 ± 2.1 | |
| 75% Corn starch / 10% sodium caseinate / 15% water | 9.0 ± 0.7 | 30.7 ± 1.9 | 25.6 ± 1.8 | |
| 70% Corn starch / 15% sodium caseinate / 15% water | 11.8 ± 1.1 | 26.9 ± 1.6 | 26.4 ± 1.9 | |
| 60% Corn starch / 25% sodium caseinate / 15% water | 14.9 ± 1.2 | 20.2 ± 2.2 | 28.0 ± 2.3 | |
| 55% Corn starch / 30% sodium caseinate / 15% water | 19.2 ± 1.7 | 17.1 ± 1.3 | 28.8 ± 2.5 | |
| 45% Corn starch / 40% sodium caseinate / 15% water | 28.0 ± 2.5 | 13.3 ± 1.2 | 29.5 ± 2.2 | |
| 47.5% Corn starch / 47.5% sodium caseinate / 5% water | 30.2 ± 2.6 | 22.0 ± 0.4 | 30.1 ± 2.7 | |
| 45% Corn starch / 45% sodium caseinate / 10% water | 32.6 ± 2.5 | 21.4 ± 0.2 | 29.0 ± 2.5 | |
| 42.5% Corn starch / 42.5% sodium caseinate / 15% water | 34.0 ± 1.8 | 20.7 ± 0.5 | 27.7 ± 1.9 | |
| 40% Corn starch / 40% sodium caseinate / 20% water | 38.0 ± 3.2 | 17.8 ± 0.3 | 25.9 ± 2.3 | |
| 37.5% Corn starch / 37.5% sodium caseinate / 25% water | 37.1 ± 1.9 | 13.0 ± 0.3 | 24.0 ± 2.2 | |

(*Continued*)

**TABLE 3-2** *Continued*

| Components | % Elongation | Tensile Strength (MPa) | Young's Modulus (MPa) | References |
|---|---|---|---|---|
| 35% Corn starch / 35% sodium caseinate / 30% water | 39.5 ± 0.6 | 11.1 ± 1.0 | 21.7 ± 2.4 | Arvanitoyannis and Biliaderis (1998) |
| 90% Soluble starch / 0% sodium caseinate / 10% water | 2.5 ± 0.3 | 38.5 ± 3.4 | – | |
| 80% Soluble starch / 10% sodium caseinate / 10% water | 4.4 ± 0.3 | 33.6 ± 4.3 | – | |
| 70% Soluble starch / 20% sodium caseinate / 10% water | 7.2 ± 0.6 | 28.2 ± 3.1 | – | |
| 60% Soluble starch / 30% sodium caseinate / 10% water | 10.0 ± 1.2 | 23.1 ± 2.2 | – | |
| 50% Soluble starch / 40% sodium caseinate / 10% water | 13.6 ± 1.5 | 19.3 ± 2.1 | – | |
| 47.5% Soluble starch / 47.5% sodium caseinate / 5% water | 2.0 ± 0.1 | 22.1 ± 1.2 | – | |
| 45% Soluble starch / 45% sodium caseinate / 10% water | 6.3 ± 0.5 | 19.5 ± 2.2 | – | |
| 40% Soluble starch / 40% sodium caseinate / 20% water | 13.0 ± 1.1 | 17.3 ± 2.1 | – | |
| 35% Soluble starch / 35% sodium caseinate / 30% water | 19.0 ± 2.0 | 12.2 ± 1.1 | – | |
| 50% Whey powder / 50% sodium caseinate | 64.5 ± 26.8 | 14.5 | – | Cho et al. (2002) |

| | | |
|---|---|---|
| 60% Whey powder / 40% sodium caseinate | 87.8 ± 13.5 | 7.9 ± 1.4 | – |
| 70% Whey powder / 30% sodium caseinate | 128.0 ± 18.8 | 4.7 ± 1.3 | – |
| 50% Whey powder / 50% sodium caseinate | 2.6 ± 0.7 | 26.8 ± 3.8 | – |
| 60% Whey powder / 40% sodium caseinate | 4.5 ± 0.6 | 17.0 ± 0.9 | – |
| 70% Whey powder / 30% sodium caseinate | 3.2 ± 0.7 | 14.0 ± 1.0 | – |
| 4% Sodium caseinate | 62.95 ± 10.61 | 3.10 ± 0.22 | – |
| 8% Sodium caseinate | 69.19 ± 10.04 | 3.27 ± 0.25 | – |
| 8% Whey protein isolate | 22.46 ± 6.61 | 5.26 ± 0.54 | – |
| 12% Whey protein isolate | 25.14 ± 6.76 | 5.42 ± 0.29 | – |
| 4% Gelatin | 45.26 ± 3.6 | 5.69 ± 0.02 | – |
| 8% Gelatin | 89.69 ± 3.21 | 6.60 ± 0.253 | – |

(FT-IR) spectra showed that the effective degradation began at $\sim300°C$ with the formation of gaseous products such as $CO_2$ and $NH_3$, suggesting that the reaction mechanism included at the same time the scission of the $C–N$, $C(O)–NH$, $C(O)–NH_2$, $–NH_2$ and $C(O)–OH$ bonds of the proteins. The suggested mechanism of reaction was supported by the high values of the activation energy ($E > 100$ kJ/mol), which are probably associated with a process that occurred by random scission of the chain (Barreto et al., 2003a).

Although binary systems, such as starch/water and starch/sugars, have been quite extensively studied (Trommsdorff and Tomka, 1995), a three-component system tends to become even more complicated with regard to the interactions between the different components. It was previously shown that the gelatinized starch–water interactions are strong and particularly localized at the early stages of sorption whereas, at high water contents ($>20\%$), a certain proportion of water exhibited liquidlike properties. Sodium caseinate was preferred over casein for use in the preparation of blends with starch because it has a higher water uptake than casein ($3–7\%$ higher when conditioned at the same RH). Therefore, water will be more homogeneously distributed throughout the entire blend mass, which may favorably influence the mechanical properties of the blend. The presence of water and sugars had a significant plasticizing effect on starch and on NaCas. According to the extent of the induced plasticization, the sugars could be classified in the order glycerol $<$ sorbitol $<$ xylose $<$ sucrose.

A general observation for all DMTA and DTA traces is that the incorporation of sugars, in conjunction with the presence of water within the starch and/or the protein matrix, resulted in substantial broadening of the tan peak or of the step transition. The limited plasticizing effect of sugars such as sucrose and xylose on starch/water blends, reported elsewhere (Kalichevsky et al., 1993) and attributed to the preferential hydration of sugar molecules, was not confirmed in our case. On the contrary, sucrose and xylose had an even more pronounced plasticizing effect than glycerol and sorbitol on starch/water blends provided that their content did not exceed 15%. The plasticization of the composite food matrix with polyols or glycerol could possibly be due to changes in the polymer network, mainly related to the creation of highly mobile regions, which allow even more pronounced moisture uptake (Cherian et al., 1995).

No double peaks were recorded below 15% sugar content, implying that the starch/NaCas blends do not phase separate. When the polyol content exceeded the threshold of 15%, double peaks were recorded as previously found for natural and synthetic polymers (Bazuin and Eisenberg, 1986). This behavior is indicative of component incompatibility in the blend (i.e., between starch and polyol). The previously observed high- and low-temperature peaks (recorded by dynamic mechanical analysis [DMA]) in the case of binary (gluten–glycerol or gluten–sucrose) or ternary (gluten–glycerol–sucrose/sorbitol) systems (Cherian et al., 1995) was not confirmed by our experiments (DTA and DMTA) involving starch–NaCas–plasticizer systems.

The interactions of molecules in the wheat starch–water or corn starch–water–sugar systems may be attributed to the interactions between hydroxyl groups of starch chains, starch–water, and starch–sugar molecules, but also to sugar–sugar

or water–sugar interactions (Tolstoguzow, 1994). The possibility of hydrogen bonding of starch within the blends increases considerably with the introduction of comparatively small molecules such as water and sugars. Previous studies on protein–protein (casein–ovalbumin, casein–soybean globulin), water, and protein–polysaccharide systems have shown that the compatibility of the blend components is greatly affected by thermal treatment or their previous thermal history (Tolstoguzow et al., 1985). It was also found that the protein–polysaccharide systems are characterized by limited compatibility between their components, occasionally resulting in phase separation.

The influence of NaCas on the thermal and rheological properties of starch gels at different concentrations and from different botanical sources was evaluated. In NaCas–starch gels, for all starches with the exception of potato starch, the NaCas promoted an increase in the storage modulus and in the viscosity of the composite gel when compared with starch gels. The addition of NaCas resulted in an increase in the onset temperature, the gelatinization temperature, and the end temperature, and there was a significant interaction between starch and NaCas for the onset temperature, the peak temperature, and the end temperature. Microscopy results suggested that NaCas promoted an increase in the homogeneity of the matrix of cereal starch gels (Bertolini et al., 2005).

In DSC analysis, the samples containing NaCas showed a decrease in the enthalpy of gelatinization. Statistical analysis of DSC data showed that there is no significant interaction between starch and NaCas addition, suggesting that NaCas addition had the same effect in decreasing the enthalpy for all starches. In samples with NaCas addition, a shift in the gelatinization peak was observed, with increases in the onset temperature, the peak gelatinization temperature, and the end temperature, in agreement with the results obtained by Erdogdu et al. (1995) for casein–wheat starch samples.

Changes in the gelatinization onset and peak temperatures appeared to be greater in cereal starches, even if the changes did not always follow this trend. In contrast to the wheat and rice starch samples, the endothermic peak at $100°C$ (relative to the amylase–lipid complex in the cereal starch samples) was not observed in the NaCas–starch samples. However, it is not clear whether these results were, at least in part, caused by a dilution effect. It has been reported that the changes in the thermal behavior of starch caused by the addition of nonstarch polysaccharide solution to the starch is markedly high at starch/solvent ratios of 1 : 10 (or above) and that the end temperature increases as the nonstarch polysaccharide concentration increases in the system (Tester and Sommerville, 2003).

There has long been debate regarding the homogeneous distribution of water in binary and ternary systems, particularly at a microstructural level. Although several new methods such as CP-MAS and nuclear magnetic resonance (NMR) imaging have been employed, no conclusive evidence has yet been published regarding this phenomenon. Therefore, in our study we assume that our binary or ternary blends are characterized by a homogeneous distribution of water. In all blends examined, a single glass transition was detected for the polymeric constituents (starch–caseinate blends), presumably due to the close proximity of the $T_s$ (Glass Transition

Temperature) values of the individual components and a similar plasticization response in the presence of water and other polyols. The $T_g$ of our binary system based on soluble starch/NaCas decreased as water content increased due to plasticization of the polymer blend. In general, sorbitol, despite its greater molecular weight, exhibited a more pronounced plasticizing effect (greater temperature depression) than glycerol on the polymer matrix. This is in agreement with other findings on starch-based polymer blends (Arvanitoyannis et al., 1996; Psomiadou et al., 1996).

Pullulan, NaCas, and their mixture in a ratio of 1 : 1 (w/w) were dissolved in distilled water under continuous stirring to obtain casting solutions of either 4% (w/w) concentration for determination of the moisture sorption isotherms or 7.5% (w/w) for preparing specimens for DSC and DMTA. The polyol-containing samples were prepared by adding sorbitol (15% or 25% db) to the polymer solutions. The solutions were then filtered through a coarse glass filter to remove any unsolubilized material (usually less than 0.5% of the dry initial matter), vacuum degassed to remove air bubbles, and cast on plastic frames. They were subsequently stored in an oven at 35°C and allowed to dry slowly. Bilayer films were prepared by successive casting of NaCas solutions onto preformed pullulan films.

In addition to the plain systems of pullulan and NaCas, the study of the composite films produced by blending or laminating both polymers could be of great interest, because this approach exploits the advantages of the distinct functional characteristics of the film-former components. Thus, the behavior of blends and bilayers was also studied by means of DMTA and DSC in the context of comparison with the plain polymer systems. As expected, bilayer films containing 25% sorbitol showed two distinct peaks corresponding to pullulan and NaCas alone. Peaks were sharper than in blend samples and their locations were near those of pure polymers.

Surprisingly, only one tan δ peak located near to the peak of pullulan was observed in bilayer systems free of sorbitol or containing 15% polyol. This is probably due to the difficulty of assigning a peak after the first one, since the DMTA signal after the first peak was very noisy. The transition temperatures corresponding to the two distinct a-relaxations observed in blend and bilayers with 25% sorbitol were determined and fitted separately to the G–T equation (Kristo and Biliaderis, 2006).

The $T_g$ values of starch–NaCas blends are presented in Table 3-3.

### 3.4.3 Irradiation and Gas Permeability

Gamma irradiation was found to be an effective method for the improvement of both barrier and mechanical properties of edible films and coatings based on calcium and sodium caseinates alone or combined with some globular proteins. Our current studies concern the influence of gamma irradiation on the physical properties of calcium caseinate–whey protein isolate–glycerol (1 : 1 : 1) solutions and gels used for film preparation (Ciesla et al., 2006).

Irradiation of solutions was carried out with cobalt-60 gamma rays at doses of 0 and 32 kGy. The increase in the viscosity of solutions was found after irradiation was connected to induce crosslinking. Lower viscosity values were detected, however, after heating of the solutions irradiated with a 32 kGy dose than after

**TABLE 3-3  Glass Transition Temperature ($T_g$) of Starch–Sodium Caseinate Blends[a]**

| Components | $T_g$ (°C) | | |
|---|---|---|---|
| | DTA | DMTA | MTA |
| 85% Corn starch / 0% sodium caseinate / 15% water | $61.2 \pm 1.3$ | $62.0 \pm 1.4$ | $64.9 \pm 1.4$ |
| 80% Corn starch / 5% sodium caseinate / 15% water | $62.9 \pm 0.9$ | $63.5 \pm 0.8$ | $67.2 \pm 1.6$ |
| 75% Corn starch / 10% sodium caseinate / 15% water | $64.5 \pm 1.2$ | $65.2 \pm 1.6$ | $70.0 \pm 1.3$ |
| 70% Corn starch / 15% sodium caseinate / 15% water | $66.0 \pm 1.4$ | $67.0 \pm 1.3$ | $73.8 \pm 1.2$ |
| 60% Corn starch / 25% sodium caseinate / 15% water | $68.0 \pm 0.9$ | $68.6 \pm 0.7$ | $75.2 \pm 1.4$ |
| 55% Corn starch / 30% sodium caseinate / 15% water | $69.1 \pm 1.1$ | $70.0 \pm 1.2$ | $78.3 \pm 1.5$ |
| 45% Corn starch / 40% sodium caseinate / 15% water | $70.9 \pm 1.5$ | $71.5 \pm 1.4$ | $81.2 \pm 1.6$ |
| 47.5% Corn starch / 47.5% sodium caseinate / 5% water | $122.0 \pm 2.1$ | $122.8 \pm 2.2$ | $134.5 \pm 1.0$ |
| 45% Corn starch / 45% sodium caseinate / 10% water | $93.5 \pm 1.8$ | $94.7 \pm 1.5$ | $106.2 \pm 1.7$ |
| 42.5% Corn starch / 42.5% sodium caseinate / 15% water | $71.3 \pm 1.9$ | $70.6 \pm 1.0$ | $86.4 \pm 1.6$ |
| 40% Corn starch / 40% sodium caseinate / 20% water | $54.5 \pm 1.5$ | $55.2 \pm 1.4$ | $67.8 \pm 1.5$ |
| 37.5% Corn starch / 37.5% sodium caseinate / 25% water | $40.4 \pm 2.0$ | $39.6 \pm 1.6$ | $54.5 \pm 1.8$ |
| 35% Corn starch / 35% sodium caseinate / 30% water | $19 \pm 1.5$ | $20.4 \pm 1.2$ | $35.0 \pm 1.7$ |
| 78% Wheat starch / 2% sodium caseinate / 17% water | $56.4 \pm 0.8$ | $54.9 \pm 1.5$ | $60.3 \pm 1.7$ |
| 71% Wheat starch / 12% sodium caseinate / 17% water | $57.6 \pm 0.6$ | $58.2 \pm 0.9$ | $63.5 \pm 1.8$ |
| 65% Wheat starch / 18% sodium caseinate / 17% water | $59.2 \pm 1.1$ | $59.9 \pm 1.3$ | $66.7 \pm 1.3$ |
| 58% Wheat starch / 25% sodium caseinate / 17% water | $63.1 \pm 1.3$ | $62.0 \pm 1.2$ | $71.0 \pm 1.5$ |
| 51% Wheat starch / 32% sodium caseinate / 17% water | $65.9 \pm 0.9$ | $67.2 \pm 1.4$ | $74.2 \pm 1.6$ |
| 43% Wheat starch / 40% sodium caseinate / 17% water | $69.3 \pm 1.2$ | $70.4 \pm 1.1$ | $77.5 \pm 0.9$ |
| 28% Wheat starch / 55% sodium caseinate / 17% water | $74.6 \pm 1.1$ | $76.2 \pm 0.8$ | $81.9 \pm 1.4$ |
| 48% Wheat starch / 48% sodium caseinate / 4% water | $114.6 \pm 2.1$ | $112.5 \pm 1.8$ | $119.5 \pm 1.8$ |

(*Continued*)

**TABLE 3-3**    *Continued*

| Components | $T_g$ (°C) | | |
| --- | --- | --- | --- |
| | DTA | DMTA | MTA |
| 46% Wheat starch / 46% sodium caseinate / 8% water | 95.6 ± 1.8 | 98.0 ± 1.5 | 107.5 ± 1.2 |
| 42.3% Wheat starch / 42.5% sodium caseinate / 15% water | 66.8 ± 1.7 | 64.3 ± 0.9 | 75.2 ± 1.4 |
| 40% Wheat starch / 40% sodium caseinate / 20% water | 49.7 ± 1.8 | 51.2 ± 1.7 | 59.4 ± 1.5 |
| 37% Wheat starch / 37% sodium caseinate / 26% water | 33.2 ± 1.5 | 31.5 ± 1.3 | 41.6 ± 1.8 |
| 35% Wheat starch / 35% sodium caseinate / 30% water | 14.4 ± 0.7 | 21.7 ± 1.4 | 21.7 ± 1.4 |

[a]Arvanitoyannis et al. (1996); Kristo and Biliaderis (2006).

heating of the nonirradiated ones. Differences in the structure of gels resulted in different temperature–viscosity curves recorded for the irradiated and the nonirradiated samples during heating and cooling. Creation of less stiff but better ordered gels after irradiation probably arises from reorganization of the aperiodic helical phase and β-sheets, in particular from increase of β-strands, as detected by FT-IR.

Films obtained from these gels are characterized by improved barrier properties and mechanical resistance and are more rigid than those prepared from the nonirradiated gels. The route of gel creation was investigated for control and irradiated samples during heating and the subsequent cooling (Ciesla et al., 2004). The irradiation of protein solutions also improved puncture strength of films prepared with potato starch, soluble potato starch, or sodium alginate additions (at a level of 50 g/kg of total proteins). Addition of potato starch did not influence the mechanical properties of films but significantly improved barrier properties. Addition of sodium alginate improved both puncture strength and barrier properties. Addition of sodium alginate to irradiated protein solution resulted in films showing the greatest improvement in properties. Gels prepared using irradiated protein solutions mixed with calcium salt were stronger than gels prepared using nonirradiated solutions due to the preferential binding of calcium ions to the crosslinked protein network (Ciesla et al., 2006).

Stronger films with improved barrier properties were prepared from irradiated solutions than from nonirradiated ones, as shown by the larger puncture strength and smaller water vapor permeability. Simultaneously, smaller deformation values and larger viscoelasticities indicate higher rigidity of the irradiated films compared to the nonirradiated ones. Statistical analysis showed that all the functional properties measured for all the irradiated films differ significantly from those determined for the control films. Puncture tests were carried out using a Stevens LFRA Texture Analyzer Model TA/100 (Texture Technology Corporation, Scarsdale, NY, USA) according to the method described by Gontard et al. (1992) and Brault et al. (1997).

A cylindrical probe (2 mm in diameter) was moved perpendicularly to the film surface at a constant speed (1 mm/s) until it passed through the film. Strength and deformation values at the puncture point were used to determine the hardness and deformation capacity of the film. Force–deformation curves were recorded. The puncture strength was related to the film thickness to avoid any variations associated with inhomogeneity in thickness. For this purpose, the measured value was divided by the film thickness (measured directly at the probe path). Viscoelastic properties were evaluated using the force relaxation curves. The same procedure was applied, but the probe was stopped and maintained at 3 mm deformation (Ciesla et al., 2006).

Control and ultraviolet (UV)-irradiated (253.7 nm, 51.8 J/m$^2$) films were evaluated for tensile strength, total soluble matter, water vapor permeability, and Hunter *L*, *a*, and *b* color values. UV treatment increased the tensile strength of gluten, zein, and albumin films, suggesting the occurrence of UV radiation-induced cross-linking within film structures. For caseinate films, UV-curing did not affect tensile strength but substantially reduced total soluble matter. Small but significant decreases in total soluble matter were also noted for UV-treated zein and albumin films. UV irradiation reduced water vapor permeability of albumin films but did not affect water vapor permeability of the other types of films. Gluten, albumin, and caseinate films had increased yellowness as a result of UV treatment. In contrast, UV treatment decreased the yellowness of zein films, possibly due to destruction of zein pigments by UV radiation (Rhim et al., 1999).

The gas permeability (GP) measurements of plasticized starch/NaCas blends showed increases in GP proportional to the plasticizer content due to weakening of the intermolecular forces between adjacent polymeric chains, which facilitates chain mobility and redistribution of the originally existing voids (Arvanitoyannis, 1999). The GP of soluble starch/NaCas blends also increased proportionally to the total plasticizer content (water, glycerol, and sugars) (Arvanitoyannis and Biliaderis, 1999).

## 3.5 APPLICATIONS

Films were cut into dumbbell-shaped strips and stored at an appropriate RH for 10 days, to obtain films with different moisture contents. Film thickness was measured at three different points with a hand-held micrometer and an average value was calculated. Samples were analyzed with a TA-XT2i instrument (Stable Microsystems, Godalming, Surrey, UK) in the tensile mode, operated at ambient temperature and a crosshead speed of 60 mm/min. Young's modulus (*E*), tensile strength ($r_{max}$) and percent elongation at break (%EB) were calculated from load–deformation curves of tensile measurements. The measurements represented an average of at least eight samples. The moisture content of samples, after storage, was determined by drying at 110°C for 2 h (Kristo et al., 2007).

Optimal mechanical properties (elastic modulus of 105 MPa, tensile strength of 8–9 MPa for elongation at break about 110–125%) were obtained for HCHO/ ε-NH$_2$ ratios higher than 1.35. Protein specific water solubility was determined

from the 280 nm absorbance. For convenient crosslinker (HCHO) content, NaCas solubility can be lowered to less than 5% wt after 24 hours immersion in water (Audic and Chaufer, 2005).

The physical properties of thin films (25–30 mm) made from mixtures of NaCas and whey protein isolate (WPI) were investigated. Films were formed by mixing solutions of NaCas (2.5% w/w protein), plasticized with glycerol (NaCas–Gly) at a glycerol : protein ratio of 0.32, with WPI solutions (2.3% w/w protein), plasticized (WPI-Gly) at a glycerol : protein ratio 0.37. Tensile and water barrier properties of films formed from mixtures of NaCas–Gly and WPI-Gly were similar to those of films containing NaCas–Gly only. Films containing only WPI-Gly had higher maximum load and elastic modulus values than the mixed films. Increasing the NaCas–Gly content of the films from 25% to 100% greatly increased solubility. This increased film solubility may increase the number of food applications for protein-based films (Longares et al., 2005).

All mechanical tests were performed at 50% ± 5% RH and a temperature of 23 ± 2°C using an Instron Universal Testing Instrument Model 4301 (Canton, MA, USA) fitted with a 100 N static load cell. The films were cut into strips 25.4 mm wide and 130 mm long using a scalpel and mounted between cardboard grips (26 × 70 mm) using double-sided adhesive tape so that the final area exposed was 100 × 25.4 mm. A minimum of eight strips were prepared from each film. The tensile properties of the films were measured according to the standard testing method 882–95a (ASTM, 1985). The mounted film samples were clamped into the metal grips of the tensile geometry of the Instron and stretched at an overhead crosshead speed of 10 mm/min.

Dynamic mechanical thermal analysis of films was conducted with a Perkin Elmer apparatus DMA-7 (Norwalk, CT, USA) equipped with a cryogenic system fed with liquid nitrogen (Air Liquide, Aix-en-Provence, France). A variable-amplitude, sinusoidal mechanical stress was applied to the sample (frequency 1 Hz) to produce a sinusoidal strain of selected amplitude. The compression mode of deformation was chosen for use with the sample geometry. Temperature scans from −30 to 260°C were performed at a heating rate of 3°C/min. The furnace temperature was calibrated with indium (Perkin Elmer Standard) and was flushed with dry nitrogen gas during analysis to avoid hydration of the films. The samples were dehydrated before testing to avoid the plasticizing effect of the water content. Three samples were tested for each material. During analysis, the stored values were the storage modulus ($E'$) and the loss tangent (tan δ). The glass transition temperature ($T_g$) was determined from the maximum of the tan δ peak (Khwaldia et al., 2004a).

The surface pressure (π) at equilibrium (surface pressure isotherm) and surface dynamic properties (dynamic surface pressure and surface dilatational characteristics) of diglycerol ester (diglycerol monocaprinate, diglycerol monolaurate, diglycerol monostearate, and diglycerol monooleate) and protein (NaCas) as emulsifiers, at different concentrations in the aqueous phase, were measured using tensiometry and a dynamic drop tensiometer, respectively. Alvarez Gomez and Rodriguez Patino (2007) have observed that at equilibrium the value of critical micelle concentration (CMC) decreases and the maximum surface excess ($\Gamma_{max}$) increases as the

hydrocarbon chain length increases because the hydrophobic character of the lipid also increases. The presence of a double bond in the hydrocarbon chain also increases the value of CMC and decreases that of $\Gamma_{max}$. Caseinate presents higher adsorption efficiency but the surface activity is between the values for lipids. The surface pressure isotherm of mixed systems is dependent on the emulsifier concentration and the protein/lipid ratio in the mixture. The adsorption of pure emulsifiers at the air–water interface increases with emulsifier concentration in the aqueous phase via diffusion and penetration of the emulsifier at the interface. For mixed films, the rate of adsorption depends on the concentration and composition of the mixture. Competitive or cooperative phenomena were observed during the adsorption of both emulsifiers at the interface. The surface dilatational characteristics of mixed films are viscoelastic. The surface dilatational modulus reflects the amount of emulsifier adsorbed at the interface and confirms the idea that the protein–lipid interactions at the air–water interface are somewhat weak, there even being the possibility of phase separation. The sorption curves of NaCas-based films have a sigmoid shape characteristic of water vapor-sensitive polymers such as cellulose (De Leiris, 1985) and wheat gluten (Gontard et al., 1993).

The curves showed a relatively slight slope at low water activity $a_w$. The exponential increase of equilibrium moisture contents with increasing $a_w$ indicated that water sorption in the polymer did not follow Henry's law (Rogers, 1985); that is, the solubility of water in the polymer varies with the partial pressure of water vapor (Brown, 1992).

In general, the DSC transition temperatures (when observed) fell between the onset of the $E_0$ drop and the peak $\tan \delta$ (at 3 Hz) for an unplasticized pullulan sample containing 16.4% w/w water, which is in agreement with the observations of Kalichevsky and Blanshard (1993) on amylopectin/fructose and of Biliaderis et al. (1999) on pullulan/starch blends.

The viscosity increase is in fact associated with the protein–water interactions, leading to a higher solvent immobilization than the protein–protein interaction. Similar results were obtained by Konstance and Strange (1991) for solutions of casein and caseinates in the presence of various salt types and pH.

The effects of four milk protein ingredients, namely, skim milk powder (SMP), milk protein concentrate (MPC), sodium caseinate (NaCas) and whey protein isolate (WPI), on the pasting behavior of a 10% normal rice starch or waxy rice starch solution were assessed using rheological and DSC measurements and confocal scanning laser microscopy (CSLM). It was found that all these milk protein ingredients affected the pasting behavior of the two rice starches markedly and differently. For instance, for normal rice starch, SMP and NaCas shifted the temperature of peak viscosity to higher temperatures, whereas MPC and WPI reduced the temperature of peak viscosity. For waxy rice starch, SMP, NaCas and WPI increased the temperature of peak viscosity, but MPC did not affect it. The value of the peak viscosity was also either increased or decreased, depending on the type of milk protein and its concentration. The onset temperature measured by DSC correlated very well with that measured by rheology. However, there was no correlation between the peak temperature measured by DSC and that measured by rheology (Noisuwan et al., 2008).

Starches are widely used in dairy-based food products, such as yogurt, because of their thickening and gelling properties. They are also added to dairy-based products to achieve cost savings by reducing the amount of milk protein. A systematic study of mixtures of starches and different dairy ingredients, such as SMP or whey proteins, would greatly advance our understanding of how starches and milk proteins interact in typical dairy product formulations. Despite starches being extensively studied, little is found in the literature about their pasting behavior when mixed with milk proteins. Most studies involving starches and milk proteins are related either to the heat stability of milk or to the effect of starch on the gelation of milk proteins. Tziboula and Muir (1993) studied the effect of the addition of starches of various botanical origins to skim milk and skim milk concentrates. They reported that the heat coagulation time was decreased when the concentration of added starch was increased and that the heat stability of milk and milk concentrate containing starch could be improved by modifying the molecular properties of the starches by acid hydrolysis or by crosslinking. Matser and Steeneken (1997) investigated the rheological properties of highly crosslinked waxy maize starch in aqueous suspensions of skim milk components. It was found that, although the salts present in milk did not increase the final gel strength of the starch gels, lactose did affect the gelatinization temperature of the starch.

The differences in response of 1% potato and 4% maize starch pastes to inclusion of NaCas were investigated. Pasting of the starches was performed at 95°C for 1 hour over a range of concentrations of NaCas. Caseinate levels as low as 0.01% dramatically reduced the swelling volume of potato starch and hence the viscosity of the system. Since addition of sodium chloride shows similar effects, it appears that caseinate acts through a nonspecific ionic strength effect. The influence of caseinate on maize starch was less clear since it depended on the solvent medium. In distilled, deionized water, there was an increase in viscosity with increasing caseinate concentration, which may simply be explained by a contribution of the caseinate to the viscosity of the continuous phase. However, in 0.1 M, pH 7.0 buffer the results suggest that caseinate may inhibit retrogradation as the viscosity of the system after aging is reduced by its inclusion. It is suggested that phase separation between starch and caseinate is encouraged at high salt concentrations. As a consequence, both starch granule swelling and subsequent retrogradation are discouraged by caseinate in the buffer system, but not when pasting is carried out in distilled, deionized water (Kelly et al., 1995).

It may be concluded that potato starch is unique in its response to low levels of electrolyte and that the very large NaCas effect is related to this rather than a specific protein–starch interaction. Potato starch is known to contain a high level of phosphate groups compared with other starches (Swinkels, 1985; Muhrbeck and Tellier, 1991). It will, therefore, have a significant polyelectrolyte character. It seems probable that the dramatic ionic strength dependence is due to Donnan effects and that the gelatinized potato starch granule is behaving as a "super-swelling" polyelectrolyte gel maintained by a relatively low density of entanglements between amylopectin molecules. The effect of caseinate on maize starch is less clear.

The large viscosity reduction reported with potato starch was not repeatable and the solvent medium seemed to play an important part in determining the effects

observed. There was a higher viscosity in buffer than in water in the absence of caseinate, suggesting that the extent of granule swelling was greater in buffer. This could reflect the lower pH (5.2) of starch alone pasted in water. In addition, in the pH 7 buffer sodium caseinate addition had no apparent effect on fresh paste viscosity. In distilled, deionized water, however, the viscosity of the fresh system increased steadily with increasing caseinate concentration. The lack of change in viscosity with increasing NaCas in buffer may reflect a slight decrease in starch swelling volume. This decrease in swelling volume would compensate for the increase in viscosity of the continuous phase with increasing caseinate concentration. On aging, maize starch will retrograde far more readily than potato starch (Kelly et al., 1995).

## 3.6  COMPARISION BETWEEN SODIUM CASEINATE AND OTHER EDIBLE FILMS

The plasticizer size and the effectiveness of the interaction between plasticizer and protein are important factors in determining the physical properties of plasticized NaCas films. Similar ideas have been invoked in the literature to explain the differences in film strength and permeability of other plasticized biopolymer systems, including gamma-irradiated caseinate (propylene glycol and triethylene glycol) (Mezgheni, 1998), whey/protein (glycerol vs. sorbitol) (McHugh and Krochta, 1994), and grain/protein (glycerol vs. PEG) (Park et al., 1994) films. The ability of the plasticizer to change the physical and water permeability properties of the film depends largely on the compatibility between the plasticizing material and the protein. The actual effect of two plasticizers on a protein is difficult to deduce in most of the published literature because comparisons are usually carried out on a weight protein/weight plasticizer basis, which does not necessarily take into account the properties and number of active sites on each plasticizer molecule. In addition, some properties (such as elongation) are affected by variations in film thickness (Sinew et al., 1999).

For caseinate adsorbed films, at the air–water interface the values of the surface dilatational modulus and its elastic component are similar but not identical to those for diglycerol esters. Thus, the values of the viscous component ($E_{va}$) are not zero, and the film presents viscoelastic behavior with values of $\tan \delta$ higher than zero. The increase in surface dilatational elasticity, or the decrease in the phase angle tangent, with time should be associated with adsorption of proteins at the air–water interface (Liu et al., 1999) as was observed for proteins in general at the air–water (Boss and van Viet, 2001) and oil–water (Benjamin's, 2000) interfaces. In fact, the results of time-dependent surface dilatational property measurements are consistent with the existence of protein–protein interactions which are thought to be due to protein adsorption at the interface via diffusion, penetration, and rearrangement (looping of the amino acid residues) as both the adsorption time and the protein concentration in the bulk phase increase (Alvarez and Rodriguez Patino, 2006). Films and variable experimental designs with level of factors are given in Table 3-4.

**TABLE 3-4    Films and Variable Experimental Design with Level of Factors (°C, %RH)**

| Films | Process Variables | | References |
| --- | --- | --- | --- |
| | °C | % RH | |
| WPI / glycerol (5.7 : 1) | 23 | 50 | Siew et al. (1999) |
| WPI / glycerol (2.3 : 1) | 23 | 50 | |
| WPI / sorbitol (2.3 : 1) | 23 | 50 | |
| WPI / sorbitol (1 : 1) | 23 | 50 | |
| WG / PEG (2.48 : 1) | 23 | 50 | |
| WG / glycerol (2.2 : 1) | 23 | 50 | |
| sodium caseinate / glycerol (4 : 1) | 23 | 50 | |
| sodium caseinate / glycerol (2 : 1) | 23 | 50 | |
| sodium caseinate / PEG (4.54 : 1) | 23 | 50 | |
| sodium caseinate / PEG (1.9 : 1) | 23 | 50 | |
| LDPE | 23 | 50 | |
| HDPE | 23 | 50 | |
| 0.25 Pullulan / 0.75 sodium caseinate | – | 53 | Kristo et al. (2007) |
| 0.625 Pullulan / 0.375 sodium caseinate | – | 53 | |
| 0.75 Pullulan / 0.25 sodium caseinate | – | 53 | |
| 0.375 Pullulan / 0.625 sodium caseinate | – | 53 | |
| 0.5 Pullulan / 0.5 sodium caseinate | – | 53 | |
| 0.75 Pullulan / 0.25 sodium caseinate | – | 75 | |
| 0.625 Pullulan / 0.375 sodium caseinate | – | 75 | |
| 0.5 Pullulan / 0.5 sodium caseinate | – | 75 | |
| 0.375 Pullulan / 0.625 sodium caseinate | – | 75 | |
| 0.25 Pullulan / 0.75 sodium caseinate | – | 75 | |

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# Novel Plastics and Foams from Starch and Polyurethanes

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## 4.1 INTRODUCTION

Worldwide potential demand for replacing petroleum-derived raw materials by renewable resources in the production of valuable biodegradable polymeric materials is significant from both social and environmental viewpoints (Mohanty et al., 2000; Lu et al., 2004; Yu et al., 2006). Among the several candidates including aliphatic polyesters, natural polymers, and their derivatives, starch—a polysaccharide obtained in granular form from corn, cereal grain, rice, and potatoes—is one of the most promising materials for biodegradable polymeric materials, due to its easy availability and low price (Wang et al., 2003; Halley, 2005). The starch granule is essentially composed of two main polysaccharides of amylose and amylopectin (see Scheme 4-1). Amylose is a linear molecule with an extended helical twist and generally has a molecular weight 1.0–1.5 million. Amylopectin is a branched molecule with a
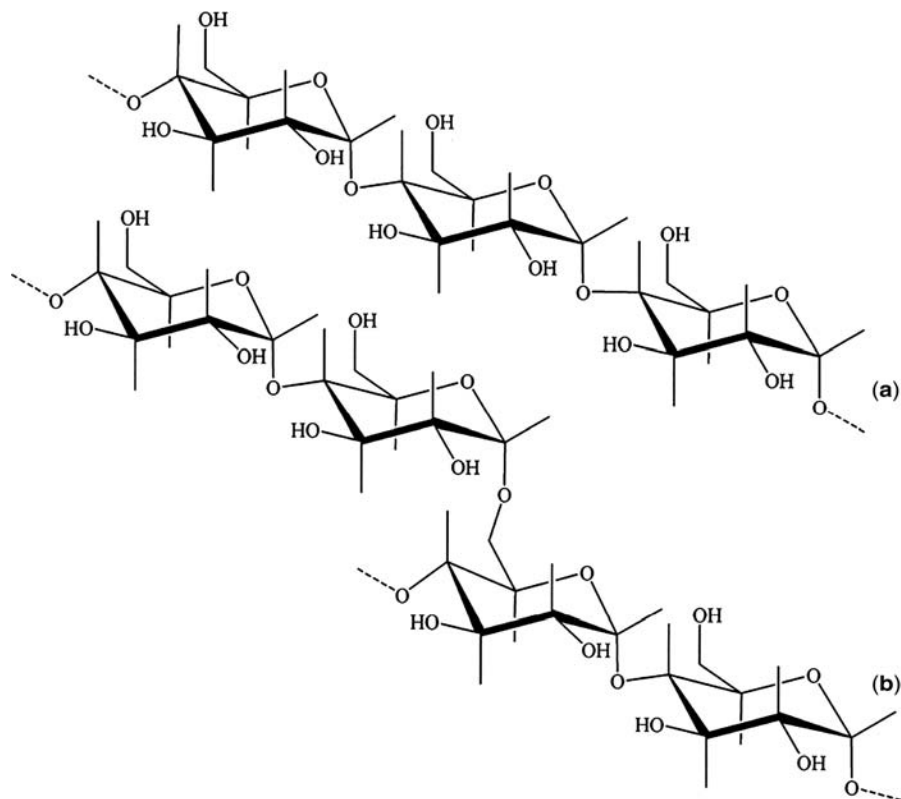
**Scheme 4-1**   Chemical structure of amylose (a) and amylopectin (b) (Wang et al., 2003).

much higher molecular weight in the range 50–500 million. Starch has been widely used in several nonfood sectors, most notably in the sizing and coating of papers, as an adhesive, as a thickener, and as a "green strength" additive to simple composite materials (Petersen, 1999). With the increased interest of biobased polymeric materials as an alternative to those produced from nonrenewable resources, research and development on starch-based materials used for plastics and foams has attracted much attention (Guan and Hanna, 2004; Lu et al., 2005a, 2006; Xu and Hanna, 2005).

Polyurethane plastics were first synthesized by Otta Bayer and co-workers in 1937 and were introduced into the market in the late 1940s (Oertel, 1994). Polyurethane, consisting of soft segments (hydroxyl-terminated oligomers) and hard segments that are the result of the introduction of short diols or diamine chain extenders with diisocyanates forming urethane or urea linkages, is a unique material that offers the elasticity of rubber combined with the toughness and durability of metals. The availability of polyurethane in a very broad hardness range allows it to replace rubber, plastic, and metal with favorable abrasion resistance and physical

properties. Due to their high performance, wide variety of raw materials, and adaptable synthetic techniques, the polyurethanes have been widely used in many applications, such as foam, cast resin, coatings, adhesives, and sealants (Król, 2007). In recent years, combinations of natural polymers with synthetic polymers have been used in many scientific disciplines because these possess better physical properties and biocompatibility than do the individual components themselves. The renewable starch-based systems are traditionally of low cost but suffer from poor processability and final product properties. Whereas the synthetic biodegradable polymers are traditionally easier to process and have excellent properties, their cost is high. Thus synergizing the advantages of starch-based and synthetic biodegradable polymers represents one key strategy for creating more applications and larger markets for biodegradable polymeric materials with high performance (Halley, 2005). The purpose of this chapter is to summarize some issues of the manufacturing processes, properties, and potential applications of biodegradable starch/polyurethane-based materials.

## 4.2   STARCH-FILLED POLYURETHANE ELASTOMERS AND PLASTICS

The presence of many hydroxyl groups in starch granules makes it a good filler for reacting with isocyanate groups of polyurethane, resulting an increase in the interfacial adhesion between the starch granules and polyurethane matrix. Chen and Li (1997) synthesized starch-filled (10–30 wt%) polyurethane sheets with good elasticity recovery by reacting a mixture of starch and poly(tetramethylene oxide) (PTMEG, $M_w = 2000$) with toluene diisocyanate (TDI). After one month of embedment under soil, the strength of the moldy sheets containing starch decreased by 20–40%, suggesting better biodegradability of the starch-modified polyurethanes than in those without starch. In addition to better biodegradation, the phosphate starch-filled polyurethane sheets also showed improved flame resistance when compared with pure polyurethane (Li et al., 1999). For polyurethane elastomers prepared using poly(propylene glycol) (PPG, $M_w = 2000$) as the soft segment and starch as a multifunctional crosslinker, the materials exhibited high mechanical properties when compared with polyurethanes using 1,1,1-trimethylolpropane (TMP) as the crosslinker. The tensile strength and elongation at break increased with increasing starch content. The filled polyurethanes exhibited two glass transitions, whereas only one glass transition temperature ($T_g$) was observed for the TMP-based polyurethane, indicating phase separation between starch–TDI and PPG–TDI segments. Greater biodegradability was observed in the starch-based polyurethanes than in the TMP-based ones (Desai et al., 2000).

The polyester-based polyurethanes are much more susceptible to biodegradation than those derived from polyether diols (Huang, 1989). Degradation studies indicated that when the polyols used were poly(hexamethylene adipate) or polycaprolactone triol (PCL) diols, the resulting polyurethanes exhibit maximum biodegradation rates under composting conditions. Surface hydrophobicity, which is related to

adhesion of bacteria on the polymer surface, is considered to be a factor in biodegradation rate under composting conditions (Huang et al., 1981; Kim and Kim, 1998).

For PCL/4,4-diphenylmethane diisocyanate (MDI)-based polyurethane filled with various amounts of starch granules (Ha and Broecker, 2002, 2003), the starch granules were well dispersed as a grafted state in the continuous polyurethane phase to form a three-dimensional network as shown in Scheme 4-2. The grafted proportion of polyurethane to starch granules increased to a maximum when the starch content was about 20 wt%, resulting in increased tensile strength and elongation for the resulting materials. However, these properties decreased rapidly with a further increasing starch content, caused by the phase separation between starch granules and polyurethane phase, the lower grafting percentage, and the fracturing of the starch granules.

Renewable resource (castor oil)-based polyurethane materials filled with starch of 5–25 wt% were synthesized and investigated by Swamy and Siddaramaiah (2003). The sheets obtained were tough, rigid, and opaque. It was observed that incorporating starch into castor oil-based polyurethane improved the physicomechanical properties of the resulting materials because of the presence of multifunctional starch in the polyurethane and the formation of extensive hydrogen bonds



Divided starch granule

Textures of the fractured polyurethane phase, viewing an alignment of the polyurethane chains toward the surface of the granules
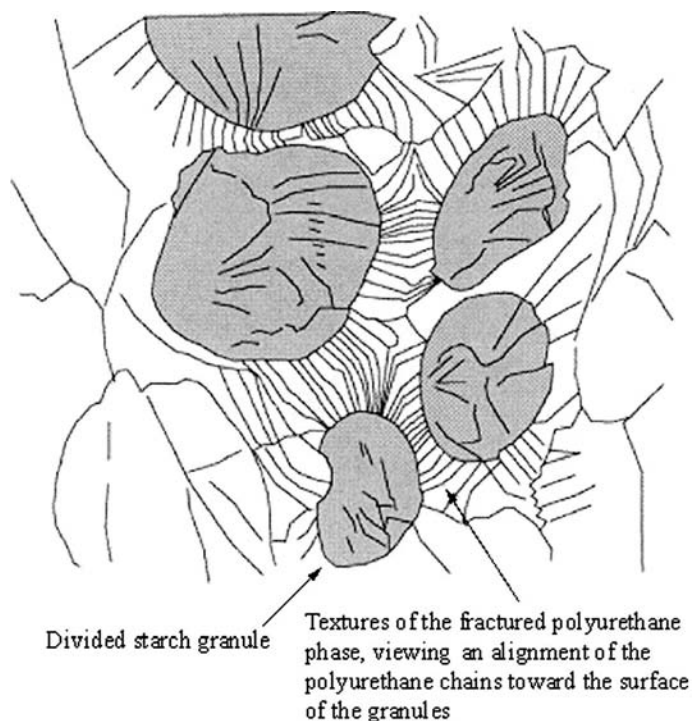
**Scheme 4-2**   Sketch of the surface textures for the starch granule-filled polyurethane (Ha and Broecker, 2003).

between polyurethane and starch. According to the authors, 5 wt% starch filler was the optimized composition to obtain high-performance material. Addition of starch into the polyurethane did not alter the crystalline region or the extent of crystallinity, but chain conformation in the amorphous region might change.

## 4.3   STARCH-FILLED POLYURETHANE FOAMS

Polyurethane (PU) foams can be considered as composite structures resulting from the controlled entrapment of the gases that are generated during the polymerization reaction between polyfunctional alcohols and polyisocyanate to form urethane linkages (Alfani et al., 1998). PU foams, compared with other materials, exhibit physical and mechanical properties related to their chemical composition and density, and are widely used in many fields as structural, cushioning, insulation, electrical, flotation, and packaging materials. High volumes of conventional polyurethane foams are produced every year, resulting in serious environmental problems. Government regulation regarding waste disposal in Europe and the United States will result in a reduction of the use of landfill and an increase of the recycling and incineration of these materials. However, recycling is difficult because of the thermosetting characteristics of polyurethanes.

Corn flour was once considered a possible source of starch for the reaction of an organic polyisocyanate with degraded starch polyoxalkylene ethers to make polyurethane foams (Otey and Mehltretter, 1965). Cunningham et al. (1991) evaluated the use of corn starch flour with different contents (5, 10, 20, 30, and 40 wt%, based on weight of polyethyl polyol) as filler-extenders in polyurethane foams, and found that 10 wt% corn flour added to the formulation served not only as filler but as a promising contributor to maintaining specific properties of polyurethane foams, especially compressive strength ($192 \pm 17 \, kN/m^2$) and insulating properties ($0.0232 \, W/mK$) as well as dimensional stability when subjected to thermal and humid conditions. They also studied the influence of unmodified starch and modified starch (20 wt% based on the polyols) on the compressive strength, density, dimensional stability, open-cell content and thermal conductivity of the resulting starch-filled polyurethane foams (Cunningham et al., 1992). The modified cornstarches used were waxy, acid-modified waxy, maltodextrin, and canary dextrin, respectively. The dextrin-filled foams exhibited higher compressive strength than that filled with starch ($141-158$ vs. $86-137 \, kN/m^2$, $196 \, kN/m^2$ for control) and responded to compressive stress like the control foam with a yield point before 10% deformation. The unmodified cornstarch-filled foams exhibited higher compressive strength than those containing either of the waxy starches ($137$ vs. $86-97 \, kN/m^2$). The open cell content of foams filled with dextrins was slight lower than that of the control (12%), foams filled with unmodified corn starch (13%), and those with modified waxy and acid-modified waxy starches (15%). According to the authors, the canary dextrin as high as 40 wt% could be incorporated into rigid polyurethane foam formulations to provide foams with similar or improved thermal stability, open-cell content, and thermal conductivity compared with the control.

Fantest is a starch–oil composite prepared by a jet cooking that uses the high temperature and turbulence within the cooker to uniformly disperse the oil component within the starch–water matrix as small droplets (Knutson et al., 1996). These droplets will not separate or coalesce, even after prolonged standing and after the product is dried. Fantest of 5–40 wt% (based on polyester polyol) blended with a polyester polyol (Lexorez 1102-50A) has been reacted with isocyanate to produce polyurethane foams, where the starch reacted with the isocyanate to form urethane bonds, resulting in a highly branched and interconnected molecular structure (Cunningham et al., 1997). Uniform mixing of the ingredients was difficult due to high viscosity of this system, resulting in the cell structure of the blend foams deteriorating with increasing Fantest content. Therefore, low-viscosity glycols, such as ethylene glycol, poly(ethylene glycol) (PEG), and propylene glycol, were used to replace the polyester polyol for preparation of polyurethane foams, in which Fantest content was maintained at 20 wt% (Cunningham et al., 1998). These three liquid glycols permitted the Fantest to blend well with the other ingredients in the foam formulations, resulting in foams with uniform, continuous cell networks with essentially transparent wall and connections as shown in Fig. 4-1. Foams containing polyethylene glycol (PEG) showed a greater number of larger cells and hence had lower densities than foams containing either ethylene or propylene glycol. NMR results indicated that oil droplets in Fantest were crosslinked with isocyanate. Intact flakes of the Fantest were observed in the foam, and their presence would make the foams more susceptible to biodegradation.

Using a mixture of starch and PCL, Alfani et al. (1998) synthesized a series of polyurethane foams with various starch contents of 0–40 wt%. The starch participated in the chemical reaction, resulting in an increase in $T_g$, an increase in material modulus and, at the same time, a reduction in density of open-cell foams obtained. The properties of the resulting open-cell foams could be modulated by adding a certain amount of PEG which, introducing flexible chains into the macromolecular structure, reduced the $T_g$ value of the materials and generated foams with higher flexibility. In contrast to the open-cell foams, Kwon and co-workers obtained foams with closed-cell structure using polyols of fully gelatinized starch (30–40 wt% based on polyols) mixed with PEG, glycerol, and 1,4-butanediol. The cell size and compressive moduli increased with NCO/OH molar ratio. The resulting foams with NCO/OH molar ratio of 0.8 exhibited the maximum absorbency for organic solvents (Kwon et al., 2007).

Many efforts have also been made to liquefy biomass in the presence of some organic reagents, such as polyhydric alcohols and phenols. It was found that polyhydric alcohols with appropriate molecular weights could be used in the liquefaction of biomass (starch, wood, etc.) with sulfuric acid as catalyst. The resulting liquefied mixtures could be used directly as polyols to prepare polyurethane foams without any additional reaction or treatment, offering a simple method to incorporate substantial amounts of biomass into the polyurethane foams (Yao et al., 1996; Lin et al., 1997; Lee et al., 2000).

Poly(ethylene glycol) shows great advantage due to its large capacity for liquefying biomass and appropriate price (Lin et al., 1997; Lee et al., 2000). Using polyols
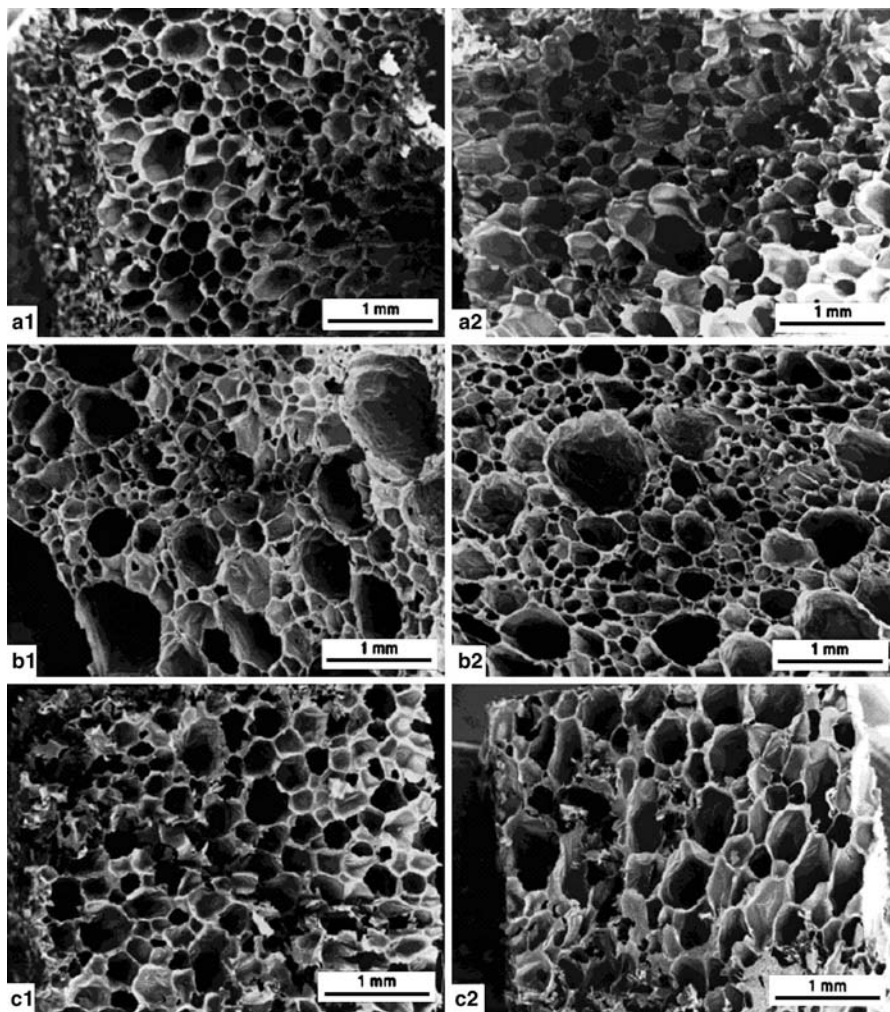
**Fig. 4-1**  Scanning electron micrographs of foams containing Fantest with glycols (a) ethylene, (b) polyethylene, and (c) propylene: (1) transverse or cross sections; (2) longitudinal sections (Cunningham et al., 1998).

prepared from liquefaction of starch in the presence of PEG ($M_w = 400$)-dominant reaction reagents, Yao et al. (1996) demonstrated the synthesis of water-absorbing polyurethane foams. It was found that about 1 wt% sulfuric acid was enough to obtain complete liquefaction even at 50 wt% starch content. The hydroxyl numbers of the liquefied starch polyols were in the range 270–369 mg KOH/g, suitable for preparation of polyurethane foams. The resulting liquefied starch polyol-based polyurethane foams exhibited continuous cell structures when a cell-opening type surfactant and a small amount of high molecular triol (poly(ether polyol), $M_w = 3000$,

functionality of 3) were employed in the formulations. The resulting foams could absorb water up to 2000 wt% within several minutes and showed good water-retention properties and substantial mechanical properties.

Starch-containing polyurethane foams were also studied by Ge and co-workers using polyols from liquefaction of the bark of *Acacia mearnsii* (BK) and corn starch (CS) in PPG, glycerol, and sulfuric acid (Ge et al., 2000). When BK was replaced partially with CS, the density and compressive strength of the foams decreased with an increase in CS content, whereas the resilience value reached its maximum when the weight ratio of CS to BK was 1 : 1, leading to possible application of the resulting materials in car-seat cushions. In addition, incorporating CS contributed to a better biodegradation of the foam materials. Using these foams as coating materials for controlled release of fertilizer, the release ratio could be controlled more effectively when BK was partially replaced with CS. Moreover, the remaining fertilizer in the foams seemed to be released completely because the foams were degradable, to some extent, by soil microorganisms (Ge et al., 2002).

## 4.4   STARCH GRAFTED WITH POLYURETHANES

The nature of brittleness caused by the relatively high glass transition temperature ($T_g$) and lack of a sub-$T_g$ main-chain relaxation (β-transition) limits the use of starch in plastics. Moreover, the brittleness increases with time due to free volume relaxation and retrogradation (Wang et al., 2003). To overcome the inherent problems with starch, Kweon and co-workers synthesized starch-*g*-polycaprolactone copolymers by a reaction of a diisocyanate-terminated polycaprolactone-based prepolymer (NCO-PCL) with corn starch at a weight ratio of starch to NCO-PCL of 2 : 1 as shown in Scheme 4-3 (Kweon et al., 2000). On grafting of NCO-PCL (35–38 wt%) prepared with TDI or 4,4-diphenylmethane diisocyanate (MDI) onto starch, the $T_g$ values of both copolymers were 238°C. However, when TDI was replaced by hexamethylene diisocyanate (HDI), the $T_g$ of the material was found to be around 195°C. On grafting NCO-PCL (PCL-1250), the degradation temperature ($T_d$) changed depending on the type of isocyanate used. The starch-*g*-PCL copolymers prepared with the MDI intermediate were most stable, to the point of thermal degradation when compared with those from TDI and HDI. Barikani and Mohammadi (2007) found that the $T_g$ values of the starch-*g*-PCL copolymers decreased with increasing percentage of the urethane prepolymer and depended on the crosslinking effect of prepolymer between two chains of starch and strong hydrogen bonding between molecules, which affected chain mobility of starch-modified urethane in different ways. Hydrophobicity of the starch grafted with a PCL-based urethane prepolymer increased with increasing amount of urethane prepolymer. According to the authors, this modified starch could be used as filler in biodegradable starch-based polyethylene due to better dispersion and compatibility.

Wilpiszewska and Spychaj synthesized starch–urethane polymers via chemical modification of potato starch with urethane and urea derivatives of HDI, as shown in Scheme 4-4, with efficiency of substitution usually above 70% (Wilpiszewska
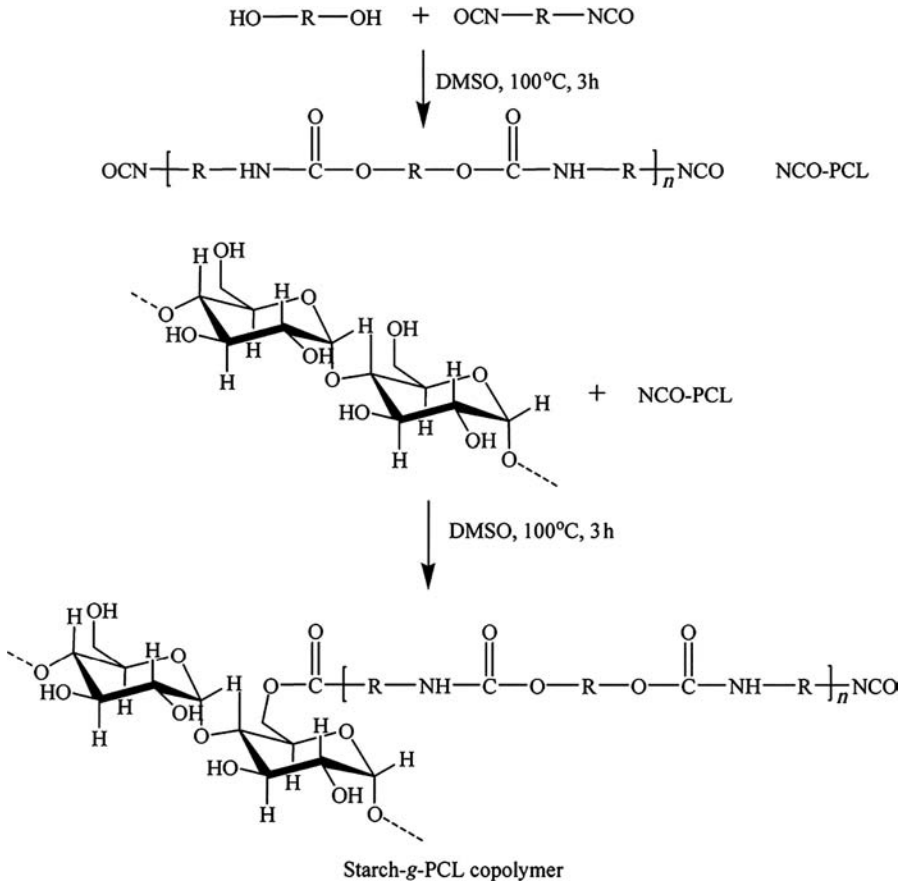
**Scheme 4-3**  Synthesis of starch-*g*-PCL copolymers (Kweon et al., 2000).

and Spychaj, 2007). The presence of additional urethane or urea bonds in short modi-fying branches can alter the properties of urethane–starch derivatives compared with those found for polymers obtained with the usually applied monoalkyl isocyanate modifiers. From the viewpoint of application, starch polymers with the degree of sub-stitution (DS) in the range of 1.6–1.8 (for theoretical DS = 2) exhibited acceptable bulk hydrophobic properties (swellability in water in the range 2.0–2.5 $cm^3/g$) and melt flow features in hot press test, making them good candidates for manufacturing through reactive extrusion processes.

## 4.5  THERMOPLASTIC STARCH/POLYURETHANE BLENDS

Beside the copolymers of starch grafted with urethane prepolymer, many plasticizers, such as glycerol, water, sorbitol, urea, amide, sugars, sodium lactate, and oligomeric
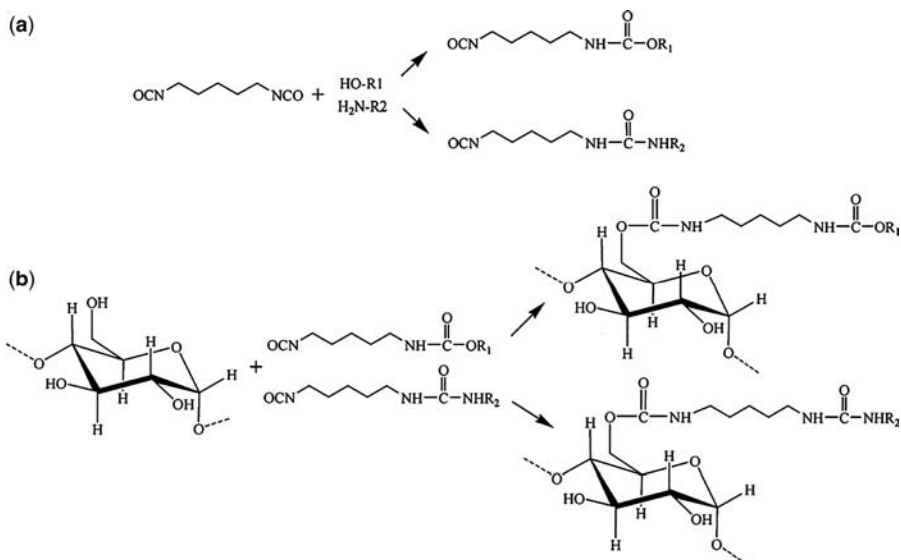
**Scheme 4-4** Reaction between HMDI and a monoalcohol or primary amine (a), and reaction between starch polysaccharide unit and HMDI/monoalcohol or HMDI/monoamine modifiers (b) (Wilpiszewska and Spychaj, 2007).

polyglycol, have also been used to lower the $T_g$ and melting temperature of the starch (van Soest et al., 1996; Lourdin et al., 1997). With the aid of plasticizer, the starch is suitable for processing through mechanical shear at elevated temperature to become an essentially homogeneous material termed thermoplastic starch (TPS) or plasticized starch (Suvorova et al., 2000). Research on thermoplastic, destructed, or melted starch has been reviewed by Roper and Koch (1990), Swanson et al. (1993), Lai and Kokini (1991), Wang et al. (2003), and Chiou et al. (2005a, b, c). Thermoplastic starch-based products are moisture sensitive and become brittle, especially after aging, when compared to typical synthetic plastics. To obtain commercially acceptable products, starch is usually blended with other materials to improve its physical properties and to minimize its water sensitivity (Chiou et al., 2005a, b, c). Examples include starch blended with other biopolymers or totally biodegradable synthetic polymers, such as starch/pectin blends (Coffin and Fishman, 1994; Fishman et al., 1996), starch/ cellulose crystalline biocomposites (Lu et al., 2005, 2006), starch/poly(vinyl alcohol) blends (Mao et al., 2000), starch/polyester blends (Bastioli et al., 1995; Fang and Hanna, 2001; Ha and Cho, 2002; Matzinos et al., 2002), and starch/ poly(D,L-lactic acid) blends (Kim et al., 1998; Park et al., 1999).

Because of the excellent properties of polyurethanes, blending starch with polyurethanes for preparation of high-performance biodegradable materials has also received much attention. In order to improve water resistance of the starch and to enhance compatibility between hydrophilic starch and hydrophobic polyurethane,

Santayanon and Wootthikanokkhan produced compression-molded blend plastics from acrylated starch (20–60 wt%) and thermoplastic polyurethane comprising of 1,4-butanediol in the hard segment and a polyester-polyol in the soft segment (Santayanon and Wootthikanokkhan et al., 2003). The blends exhibited improved water-resistance and better interfacial adhesion compared with those based on normal starch and polyurethane. However, little difference in the mechanical properties, such as tensile strength, elongation, and toughness, was observed for the blends modified with acrylated starch and with normal starch. The blends with modified starch experienced slower biodegradation than those containing normal starch.

Blend materials based on thermoplastic poly(ester-urethanes) and starch can be tailored to be biodegradable (Seidenstücker and Fritz, 1999). Seidenstücker and Fritz described a compounding procedure for production of blends consisting of thermoplastic poly(ester-urethane) (TPU) and TPS using co-rotating twin-screw extruders, and showed that the TPU/ST blends could be easily processed to give excellent flat and tubular films. Table 4-1 compared the properties of the new TPU/TPS blends with polyolefins. It can be clearly seen that many properties of the TPU/TPS blends are in the range of polyolefin properties. Further, incorporation of starch into thermoplastic poly (ester-urethane) can significantly increase the rate of biodegradation of the resulting materials. The outstanding properties of such blends, according to the authors, are summarized below:

1. They consist of high amounts of renewable resources (up to 80–85 wt%) in cases where the polyol is based upon renewable resources as well.
2. Compared with most biodegradable materials such blends have good to excellent mechanical properties that can be varied within wide limits.
3. Such blends have a favorable price range compared with other biodegradable polymers.
4. Films as well as molded parts can easily be produced.
5. Compared with polyolefin films and sheets, films made of such new blends show significantly higher steam permeability. Their oxygen permeability lies in the same range.
6. They possess a fixed morphology whereby no coalescence occurs in downstream molding processes.
7. These TPU/TPS blends can be designed to be compostable.
8. The blends show good printability and colorability.
9. They are easily weldable and sealable.
10. The blends possess high resistance to abrasion.

Conventional polyurethane products, such as coatings and adhesives, contain significant amount of organic solvents and some also contain free isocyanate monomers (Lee et al., 2006). To meet the increasing concerns about health, safety, and the environment, the conventional polyurethanes have gradually been replaced by the

**TABLE 4-1  Properties of the New TPU/TPS Blends Compared with Polyolefins and TPU/Starch Compounds Seidenstücker and Fritz (1999)**

| Properties | TPU/Native Starch[a] | TPU/TPS[a] | Polyethylene | Polypropylene |
|---|---|---|---|---|
| Tensile strength (MPa) | 16–35 | 18–25 | 8–29 | 21–37 |
| Elongation at break (%) | 4–180 | 4–800 | 40–500 | 20–800 |
| Elasticity modulus (MPa) | 100–1750 | 20–500 | 200–1400 | 1100–1300 |
| *Hardness* | | | | |
| Shore A | – | >70 | >70 | – |
| Shore D | ≈55 | – | – | – |
| Max. temperature (°C) | <80 | <80 | 60–80 | 80–120 |
| Density (g/cm$^3$) | 1.31–1.39 | 1.30–1.37 | 0.916–0.96 | 0.9–0.907 |
| Impact resistance (kJ/m$^3$) | No break at room temperature | | | |

[a]50 wt% TPU.

waterborne polyurethanes. Waterborne polyurethanes present many advantages in relation to conventional solvent-borne polyurethanes, including low viscosity at high molecular weight and good applicability (Modesti and Lorenzetti, 2001). Due to their versatility and environmental friendliness, waterborne polyurethanes are now one of the most rapidly developing and active branches of polyurethane chemistry and technology.

Wu and Zhang prepared a series of compression-molded sheets based on TPS and waterborne polyurethanes from TDI, poly(1,4-butylene glycol adipate) (PBA) and dimethylol propionic acid (DMPA) (Wu and Zhang, 2001a). When the waterborne polyurethane content was in the range of 5–30 wt%, the tensile strengths of the molded blend sheets were higher than those of starch and polyurethane, while the elongations at break were between those of the pure components and much higher than that of TPS, indicating that waterborne polyurethane could effectively improve the mechanical properties of TPS. The water resistance of the blend sheets also significantly increased with an increase in the content of waterborne polyurethane. For TPS, the $R$ value ($R$ = wet strength/dry strength) is 0.01. However, this value increased significantly to 0.24, 24 times higher than that of TPS, when 30 wt% waterborne polyurethane was incorporated. These improvements could be explained by strong interactions in the molded sheets. In this system, the waterborne polyurethane played an important role in formation of new morphology and in the performance enhancement of the blends, providing a possible application in the field of biodegradable materials. Similar results have also been observed in the casting blend systems consist of starch and polyurethane from TDI, poly(oxypropylene glycol) and DMPA (Wu and Zhang, 2001b).

In casting blends of the aqueous mixture of plasticized starch and polyester-based waterborne polyurethanes with different NCO/OH molar ratios, Cao et al. (2003) found that the thermal and mechanical properties of the starch/PU blends depend not only on the starch content but also on the microstructure of the waterborne polyurethanes. The resulting blends containing 20 wt% starch exhibit higher $T_g$ than the corresponding waterborne polyurethane and other blends with starch content higher than 50 wt%, implying that the starch in the soft segment matrix of polyurethane restricted the mobility of soft segment due to the relative strong hydrogen-bonding interaction. The polyurethane (WPU2) with higher NCO/OH molar ratio exhibited higher tensile strength than WPU1 with lower NCO/OH molar ratio, because of the formation of hard segment ordered structure. However, when starch content was lower than 50 wt%, the resulting starch blends from WPU1 exhibited higher tensile strength and elongation at break when compared with that from WPU2, because the incorporation of the appropriate content of starch not only filled the soft-segment matrix to reinforce the materials but also hindered the formation of hard-segment ordered structure, resulting in the increase of tensile strength of the starch/WPU1 blends. The blend with an optimized composition (WPU1/starch = 80/20, weight ratio) exhibited simultaneously good tensile strength (27 MPa) and elongation at break (949%).

Most polyols used for production of waterborne polyurethanes are based on petroleum-based resources. Recently, Lu et al., synthesized novel waterborne

polyurethane dispersions from rapeseed oil polyols (Lu et al., 2005b) and castor oil (Lu et al., 2005c). The use of vegetable oils to synthesize environmentally friendly waterborne polyurethanes has superb environmental credentials, such as the products being inherently biodegradable, having low ecotoxicity and low toxicity towards humans, being derived from renewable resources, and contributing no volatile organic chemicals (Erhan, 2005). Transparent films cast from waterborne polyurethane dispersions (molar ratio of NCO to OH of vegetable oil-based polyol is 2.0) exhibited high tensile strength (8–15 MPa) and elongation at break (280–520%). The extruded blend sheets show good interfacial adhesion between polyurethane and starch, as shown in Fig. 4-2, due to the hydrogen bonding interactions between the urethane groups of the polyurethane and the hydroxyl groups on starch. These interactions tend to lower the interfacial tension between polyurethane and starch, making them more compatible.

For starch/castor oil-based waterborne polyurethane blends, the tensile strength first increased with increasing polyurethane content and reached its maximum (5.1 MPa) at 15 wt% content of polyurethane, then decreased to 2.6 MPa at 30 wt% polyurethane. Simultaneously, the elongation at break increased from 120% to 176% with increasing polyurethane content from 0 to 10 wt%, and then decreased slightly to 140% with further increasing polyurethane (Lu et al., 2005c). This indicates that
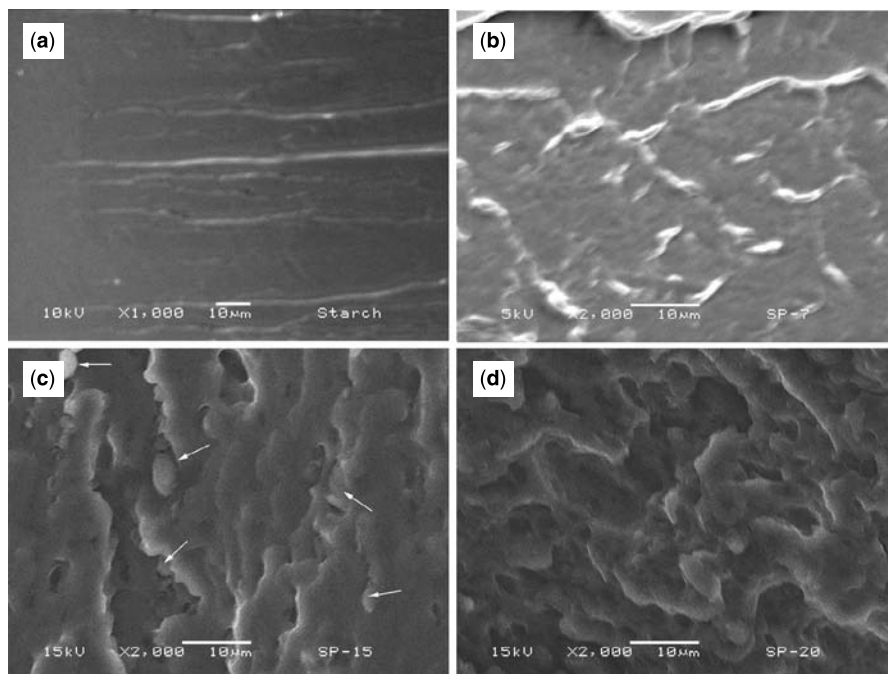


**Fig. 4-2** SEM images of thermoplastic starch (TPS)/castor oil-based waterborne polyurethane blends. (a) (TPS), (b) (blend with 7 wt% polyurethane), (c) (blend with 15 wt% polyurethane), and (d) (blend with 20 wt% polyurethane) (Lu et al., 2005c).

incorporating an appropriate content of polyurethane into starch matrix can improve the mechanical properties of the blends in both tensile strength and elongation at break. However, the mechanical behavior of these blends was different from that of the blends of both TPS/PCL (Averous et al., 2000) and TPS/PLA (Martin and Averous, 2001), whose elongations at break decreased significantly when PCL or PLA was added. After aging of 30 weeks, an increase in strength was observed for the aged blends compared with that of non-aged ones, due to the retrogradation of starch during the storage. Although there was a decrease in elongation at break after aging, the blends with 4–15 wt% PU still exhibited relatively high flexibility (elongation at break 92–121%).

The water resistance of starch can also be significantly improved by blending castor oil- or rapeseed oil-based waterborne polyurethane. The plasticized starch absorbed about 60% water at equilibrium. This value decreased with an increase of content of vegetable oil-based polyurethanes in the blends. For example, only about 25% of water uptake was observed for blends containing 50 wt% rapeseed oil-based waterborne polyurethane (Lu et al., 2005b). This can be ascribed to the presence of strong hydrogen-bonding interactions between starch and polyurethanes, which tend to stabilize and prevent the swelling of the starch in high moisture environments. The resulting blend materials show high potential for packaging applications.

## 4.6  CONCLUDING REMARKS

Research conducted in recent decades has demonstrated that incorporating starch into polyurethane imparts good physical properties and higher biodegradability on the materials. Their mechanical properties, close to those of traditional plastics such as polyethylene and polypropylene, and their improved water resistance make these materials particularly suitable for the production of films, molded items, and foams, leading to novel materials with high potential for practical application. However, the starch–polyurethane materials are still at an early stage of development with many opportunities still to be exploited—for example, the development of advanced high starch loading foams and the compatibilization between starch and polyurethane. Moreover, effective environmental assessments of the end-life materials have not been undertaken. Thus, the future development of advanced starch–polyurethane materials will rely on continued research, especially in the mechanisms and kinetics of reaction and compatibilization, advanced processing techniques, and environmental assessments.

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■■■■■ **CHAPTER 5**

# Chitosan—Properties and Application

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## 5.1 SOURCES

Chitosan is a polymer derived from chitin when the degree of deacetylation (DD) of chitin reaches values of about 50% and then becomes soluble in aqueous acidic media. The solubilization occurs by protonation of the $-NH_2$ function on the C-2 position of the D-glucosamine repeat unit, whereby the polysaccharide is converted to a polyelectrolyte in acidic media.

Chitosan is inexpensive, biodegradable, and nontoxic for mammals. This makes it suitable for use as an additive in the food industry (Koide, 1998; Shahidi et al., 1999), as a hydrating agent in cosmetics, and more recently as a pharmaceutical agent in biomedicine (Dodane and Vilivalam, 1998; Illum, 2003; Khor and Lim, 2003). This biopolymer is synthesized by an enormous number of living organisms; and, considering the amount of chitin produced annually in the world, it is the most abundant polymer after cellulose. Chitin occurs in nature as ordered crystalline microfibrils forming structural components in the exoskeletons of arthropods or in the cell walls of fungi such as *Aspergillus* and *Mucor* (Qin et al., 2006) and yeast. It is also

produced by a number of other living organisms in the lower plant and animal king-doms, serving in many functions where reinforcement and strength are required.

In industrial processing, chitin is extracted from crustaceans by acid treatment to dissolve calcium carbonate followed by alkaline extraction to solubilize proteins. In addition a decolorization step is often added to remove leftover pigments and obtain a colorless product. These treatments must be adapted to each chitin source, owing to differences in the ultrastructure of the initial materials (the extraction and pretreatment of chitin are not described here). The resulting chitin needs to be graded in terms of purity and color because residual protein and pigment can cause problems in further utilization, especially for biomedical products. By partial deacetylation under alkaline conditions, one obtains chitosan, which is the most important chitin derivative in terms of applications.

## 5.2  STRUCTURE

Chitin, poly($\beta$-(1−4)-*N*-acetyl-D-glucosamine), is a natural polysaccharide of major importance, first identified in 1884 (see Fig. 5-1).

Depending on its source, chitin occurs as two allomorphs, namely, the $\alpha$ and $\beta$ forms (Allen, 1963; Alves et al., 1999), which can be differentiated by infrared and solid-state NMR spectroscopy together with X-ray diffraction. A third allomorph $\gamma$-chitin has also been described (Allen, 1993; Anker, 2002) but, from a detailed
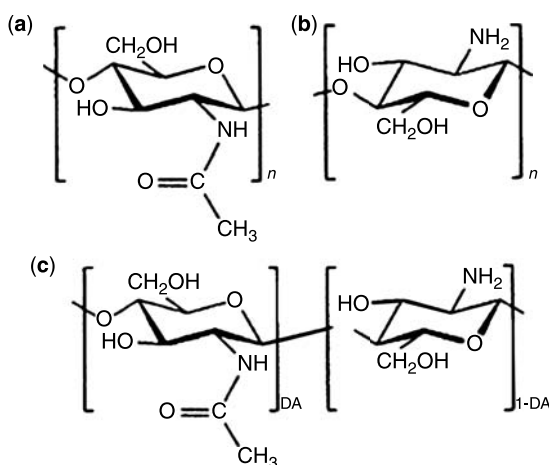


**Fig. 5-1**  Chemical structure of (a) chitin, poly(*N*-acetyl-$\beta$-D-glucosamine) and (b) chitosan, poly(D-glucosamine) repeat units. (c) Structure of partially acetylated chitosan, a copolymer characterized by its average degree of acetylation.

analysis, it seems that it is just a variant of the α family. α-Chitin is by far the most abundant; it occurs in fungal and yeast cell walls, in krill, in lobster and crab tendons and shells, and in shrimp shells, as well as in insect cuticle. It is also found in or produced by various marine living organisms. The rarer β-chitin is found in association with proteins in squid pens (Allen, 1963; Anker, 2002) and in the tubes synthesized by pogonophoran and vestimetiferan worms (Butler, 1996; Cha and Cooksey, 2001). It also occurs in *Aphrodite chaetae* (Chen, 1995) as well as in the lorica built by some seaweeds or protozoa (Debeaufort et al., 1993; Coma et al., 2002). A particularly pure form of β-chitin is found in the monocrystalline spines excreted by the diatom *Thalassiosira fluviatilis* (Debeaufort et al., 1993, 1998, 2000). To date, it has not been possible to obtain β-chitin either from solution or by *in vitro* biosynthesis.

The most important derivative of chitin is chitosan, obtained by (partial) deacetylation of chitin in the solid state under alkaline conditions (concentrated NaOH) or by enzymatic hydrolysis in the presence of a chitin deacetylase. Because of the semicrystalline morphology of chitin, chitosans obtained by solid-state reaction have a heterogeneous distribution of acetyl groups along the chains. In addition, it has been demonstrated that β-chitin exhibits much higher reactivity in deacetylation than α-chitin (Lerdthanangkul and Krochta, 1996). The influence of this distribution was examined by Aiba (1991), who showed that the distribution, random or blockwise, is very important in controlling solution properties. Reacetylation, up to 51%, of a highly deacetylated chitin in the presence of acetic anhydride gives a water-soluble derivative, whereas a heterogeneous product obtained by partial deacetylation of chitin is soluble only under acidic conditions, or is even insoluble. It was demonstrated from NMR measurements that the distribution of acetyl groups must be random to achieve the higher water solubility around 50% acetylation. Homogeneously deacetylated samples were obtained recently by alkaline treatment of chitin under dissolved conditions (Petersen et al., 1999). Toffey and Glasser, 1999 transformed chitosan films cast from aqueous acetic acid into chitin by heat treatment. Chitosan must be dissolved in an acid solution in order to activate its antimicrobial properties, and acetic acid is the best acid for this purpose (Romanazzi et al., 2005).

Chitosan is the only pseudonatural cationic polymer and thus it finds many applications that follows from this unique character (flocculants for protein recovery, depollution) (Rinaudo, 2006). An important parameter for the use of chitosan is its solubility, which depends not only on the average degree of deacetylation but also on the distribution of the acetyl groups along the main chain, in addition to molecular weight (Aiba, 1991; Kubota and Eguchi, 1997; Rinaudo and Domard, 1999). Chitosan solubility is usually tested in acetic acid by dissolving it in 1% or 0.1 M acetic acid. It has also been demonstrated that the amount of acid needed depends on the quantity of chitosan to be dissolved. The concentration of protons needed is at least equal to the concentration of $-NH_2$ units involved (Rinaudo et al., 1999). Chitosan also has good complexing ability due to the $-NH_2$ groups present in the polymer. Better chelation is related to

higher degree of deacetylation, i.e., to the content of $-NH_2$ groups, as well as to their distribution.

The cationic nature of chitosan is very important in its chelation mechanism; the affinity of chitosan follows the order:

$$Cu^{2+} \gg Hg^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+} > Co^2 \sim Ca^{2+}$$

In the solid state, chitosan is a semicrystalline polymer. Its morphology has been investigated and many polymorphs are described in the literature. Single crystals of chitosan were obtained using fully deacetylated chitin of low molecular weight.

Characteristics of particular interest are broad antimicrobial activity (Sugarcane et al., 1992), antioxidant properties (Kamala et al., 2002), use as a curing agent for color and flavor development (Park et al., 1997), and excellent film-forming ability (Kittery et al., 1998). Chitosan is able to extend storage life and to control decay of strawberries, apples, peaches, pears, kiwifruit, cucumbers, litchis, sweet cherries, and citrus fruit. The biopolymer has a dual mechanism of action: it inhibits the growth of decay-causing fungi (Allan and Headwater, 1979) and it induces defense responses in host tissues (Shibuya and Minami, 2001).

In particular, the use of chitosan as films and edible coatings to extend shelf-life and preserve quality of fruits and vegetables has received considerable attention in recent years (Shahidi et al., 1999). For use as an effective coating, the films should exhibit adequate mechanical properties and create a gas barrier. However, the aqueous acid media necessary to solubilize the chitosan present a serious drawback, particularly to the mechanical properties of the cured films, since mechanical features of chitosan films are strongly solvent-dependent: different aqueous acid media employed for chitosan dissolution generate films with variable degrees of brittleness and toughness. Several researchers have developed methods to improve the properties of chitosan using chemical and enzymatic modifications.

One strategy to improve the mechanical properties and alter the hydrophilic character of chitosan is to synthesize alkyl derivatives (Descriers et al., 1996). The alkyl moiety may reduce the inter- and intracanial hydrogen bonds, introducing plastic characteristics to the derivative, as well as improving its barrier properties against water loss (Lazaridou and Biliaderis, 2002). Besides this, there is evidence that the alkyl moiety also plays important role in increasing the antimicrobial activity of chitosan derivative (Jail et al., 2001).

Films of water-soluble quaternary salts of chitosan with different alkyl moieties were successfully obtained using diethyl sulfate as a ethylating agent. For food use, the quaternary salt represents an advance as it obviates the need for an acid medium (Britton and Assist, 2007).

Another strategy to improve chitosan properties is to form the chitosan–glucose complex (CGC), which is a better preservative than chitosan alone. Research on this complex showed superior antioxidant activity compared with chitosan/glucose alone. The antimicrobial activity of the CGC was identical to that of chitosan against the common food spoilers and pathogens such as *E. coli*, *Pseudomonas*

sop., *S. aurous*, and *B. cereus*. Thus CGC seems to be a novel natural preservative endowed with both antibacterial and antioxidant activity and may find applications in the food industry.

## 5.3 APPLICATION IN THE FOOD INDUSTRY

In native as well as modified forms both chitin and chitosan are used in a wide range of applications, such as in food, biotechnology, materials science, drugs and pharmaceuticals, and recently in gene therapy (Kop et al., 2002; Agulló et al., 2003). The biocompatibility and the biodegradability of chitosans make them a very interesting polymer for all these applications. The net catholicity and the presence of reactive functional groups (1 amino and 2 hydroxyl groups per glucose-N residue) in the molecule make chitosan an attractive bimolecular (Peasant and Tharanathan, 2007). The free amino group present in each monomeric unit affords an ammonium group, due to protonation, in aqueous acidic media. This offers scope for manipulation for preparing a broad spectrum of derivatives for specific end use applications in diversified areas such as agriculture and medicine.

In the food industry, chitosan has been studied as an antioxidant, as an antimicrobial (Prashanth and Tharanathan, 2007), for recovering soluble proteins from surimi waste (Wibowo et al., 2005), for edible coatings (Ribeiro et al., 2007), for films (Britto and Assis, 2007), for clarification of fruit juices, for control of enzymatic browning in fruits, and for purification of water (Shahidi et al., 1999). No and co-workers gave an extensive review of food applications of chitosan (No et al., 2007). Chitosan has also been used as wall material for encapsulation of some sensitive core ingredients such as lipophilic drugs (Ribeiro et al., 1999), vitamin $D_2$ (Shi and Tan, 2002), astaxanthin (Higuera-Ciapara et al., 2004), and olive oil extract (Kosaraju et al., 2006).

Chitin is widely used to immobilize enzymes and whole cells; enzyme immobilization has applications in the food industry, such as clarification of fruit juices and processing of milk when α- and β-amylases or invertase are grafted onto chitin. On account of its biodegradability, lack of toxicity, physiological inertness, antibacterial properties, hydrophilicity, gel-forming properties, and affinity for proteins, chitin has found applications in many areas other than food, such as in biosensors (Krajewska, 2004). Chitin-based materials are also used for the treatment of industrial waste (Rinaudo, 2006). Chitin can be processed in the form of films and fibers: Fibers were first developed by Austin and Brine (1977) and then by Hirano and Midorikawa (1998). The chitin fibers, obtained by wet-spinning of chitin dissolved in a 14% NaOH solution, can also after post chemical modifications give rise to a series of biofibers: chitin cellulose, chitin-silk, chitin-glycosaminoglyccus (Hirano and Midorikawa, 1998; Hirano et al., 1999). They are nonallergic, deodorizing, antibacterial, and moisture controlling (Tatsumi et al., 1991). Regenerated chitin derivative fibers are used as binders in the paper making process; the addition of 10% *n*-isobutylchitin fiber improves the breaking strength of paper (Kobayashi et al., 1992).

## 5.4  ANTIMICROBIAL PROPERTIES

The antimicrobial property of chitosan and its derivatives has received considerable attention in recent years as a potential food preservative of natural origin due to its antimicrobial activity against a wide range of foodborne filamentous fungi, yeast, and bacteria (Sagoo et al., 2002), as well as to emerging problems associated with synthetic chemical agents. The mechanism of the antimicrobial activity of chitosan has not yet been fully elucidated, but several hypotheses have been proposed. The most feasible is a change in cell permeability due to interactions between the positively charged chitosan molecules and the negatively charged components (lipopolysaccharides and proteins) of the microbial cell membranes. The cationic charge of the chitosan molecule gives rise to aggressive binding to the microbial cell surface, leading to gradual shrinkage of the cell membrane and finally death of the cell. This interaction leads to the leakage of proteinaceous and other intracellular constituents (Leuba and Stössel, 1986; Papineau et al., 1991; Sudarshan et al., 1992; Young et al., 1982; Fang et al., 1994). Other mechanisms are the interaction of diffused hydrolysis products with microbial DNA, which leads to the inhibition of mRNA and protein synthesis (Hadwiger and Loschke, 1981; Hadwiger et al., 1986; Sudarshan et al., 1992) and the chelation of metals, and essential nutrients (Cuero et al., 1991).

Chitosan shows a broad-spectrum antimicrobial activity against both gram-positive and gram-negative bacteria and fungi (Kumar et al., 2005). According to Muzzarelli et al. (1990), chitosan's antimicrobial activity against bacteria could be due to the polycationic nature of its molecule, which allows interaction and formation of polyelectrolye complexes with acid polymers produced at the bacteria cell surface (lipopolysaccharides, teichoic and teichunoric acids, or capsular polysaccharides). Chitosan-based films and coatings tested on *Listeria monocytogenes* were found to inhibit the growth of this microorganism (Coma et al., 2002). El Ghaouth et al. (1992b) showed that coatings based on 1% and 2% chitosan reduced the incidence of tomato deterioration, mainly that caused by *Botrytis cinerea*. Chitosan films were produced from a solution of starch yam (4%) and glycerol (2%) gelatinized in a viscoamylograph and with addition of chitosan at concentrations of 1%, 3%, and 5%. Films incorporating chitosan at different concentrations showed similar antimicrobial efficiency on *Salmonella enteritidis* suspension. The chitosan-containing films caused a reduction of 1 to 2 log cycles in the number of microorganisms, whereas the pure chitosan solution gave a reduction of 4 to 6 log cycles log compared to the control and starch films (Durango et al., 2005).

In a study on the mode of antimicrobial action of chitosan (250 ppm at pH 5.3) by monitoring the uptake of the hydrophobic probe 1-*N*-phenylnaphthylamine, *Escherichia coli*, *Pseudomonas aeruginosa*, and *Salmonella typhimurium* showed significant uptake, which was reduced (*E. coli*, salmonellae) or abolished (*P. aeruginosa*) by $MgCl_2$. Chitosan also sensitized *P. aeruginosa* and salmonellae to the lytic effect of sodium dodecyl sulfate. Electrophoretic and chemical analyses of the cell-free supernatants revealed no release of lipopolysaccharides or other membrane lipids. Electron-microscopic observations showed that chitosan caused extensive

cell surface alterations and covered the outer membrane with vesicular structures, resulting in the loss of barrier functions (Helander et al., 2001).

However, many other food compounds such as carbohydrate, protein, fat, minerals, vitamins, salts, and others may interact with chitosan and lead to loss or enhancement of antibacterial activity.

Devlieghere et al. (2004) studied extensively the influence of different food components (starch, protein, oils, and NaCl) on the antimicrobial effect of chitosan. For this, the media were inoculated with *Candida lambica* (2 log CFU/ml) and incubated at $7°C$ with varying chitosan concentrations (43 kDa, DD = 94%; 0%, 0.005%, and 0.01%) and with the separate addition of the following food components: starch (0%, 1%, and 30% water-soluble starch), proteins (0%, 1%, and 10% whey protein isolate), oil (0%, 1%, and 10% sunflower oil) and NaCl (0%, 0.5%, and 2%). Starch, whey protein, and NaCl had a negative effect on the antimicrobial activity of chitosan. The oil had no influence. The same authors tested the antimicrobial activity against several microorganisms at different chitosan concentrations and pH values at $7°C$ for 60 days. The results are summarized in Table 5-1.

The major postharvest losses of fruits are due to fungal infection, physiological disorders, and physical injuries (El Ghaouth et al., 1992a, b). Edible coatings might extend the storability of perishable commodities by acting as a protective barrier to reduce respiration and transpiration rates through fruit surfaces, retard microbial growth and color changes, and improve texture quality of fruits (Kester and Fennema, 1986). Studies have shown that chitosan-based coatings have the potential to increase the shelf-life of fresh fruits and vegetables, inhibiting the growth of microorganisms, reducing ethylene production, increasing internal carbonic gas, and decreasing oxygen levels (Lazaridou and Biliaderis, 2002).

Soares et al. (2007) evaluated guava subjected to four treatments (starch coating with 1.0% and 1.5% of chitosan acetic acid, starch coating, and acetic acid/starch coating) during 12 days of storage at room temperature. The skin color of the fruit remained more greenish when treated with chitosan (see Fig. 5-2) and the pulp was more consistent (see Fig. 5-3).

Geraldine et al. (2007) found that peeled garlic coated with chitosan-agar solution had a significant reduction in respiration rate compared with peeled cloves (see Fig. 5-4).

Durango et al. (2006) developed an edible antimicrobial coating based on a starch–chitosan matrix and evaluated its effect on minimally processed carrot by means of microbiological analysis. Carrot slices were immersed into four coatings (1, no coating; 2, yam starch + glycerol; 3, yam starch + glycerol + 0.5% chitosan; 4, yam starch + glycerol + 1.5% chitosan) and stored in trays wrapped with poly(vinylchloride) films at $10°C$ for 15 days. The presence of 1.5% chitosan in the coating inhibited the growth of lactic acid bacteria and total coliforms throughout the storage period (see Fig. 5-5).

Fruits and vegetables, in general, are wrapped in their own natural packaging. This barrier regulates the transport of oxygen, carbon dioxide, and moisture

**TABLE 5-1  Time for Turbidity (Days) at 7°C for Different Microorganisms in Traditional Growth Media with Different Chitosan Concentrations**

| | | Turbidity Time (days) | | | | | | | | | | |
| | | Chitosan (mg/ml) | | | | | | | | | | |
| Microorganism | pH | 0 | 40 | 60 | 80 | 100 | 200 | 250 | 300 | 400 | 500 | 750 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Candida lambica* | 5.5 | 5 | 5 | 5 | 5 | 6 | 14 | ND[a] | 40 | –[b] | – | ND |
| *Cryptococcus humiculus* | 4 | 12 | 12 | 12 | – | – | – | ND | – | – | – | ND |
| *Photobacterium phosphoreum* | 5.5 | 14 | 14 | 21 | – | – | – | ND | – | – | – | ND |
| *Pseudomonas fluorensces* | 5.5 | 8 | 18 | 28 | – | – | – | ND | – | – | – | ND |
| *Enterobacter aeromonas* | 5.5 | 39 | 47 | – | – | – | – | ND | – | – | – | ND |
| *Bacillus cereus* | 5.5 | 11 | 11 | 5 | – | – | – | ND | – | – | – | ND |
| *Brochothrix thermosphacta* | 5.5 | 5 | 5 | 5 | – | – | – | ND | – | – | – | ND |
| *Listeria monocytogenes* | 5.5 | 8 | 10 | 18 | 32 | 33 | – | ND | – | – | – | ND |
| *Lactobacillus sakei* | 5.5 | 4 | 4 | 4 | 4 | 6 | 12 | ND | 13 | 26 | 30 | ND |
| *Lactobacillus plantarum 1* | 5.0 | 24 | ND | ND | ND | 24 | ND | 49 | ND | ND | – | – |
| *Lactobacillus plantarum 2* | 5.0 | 23 | ND | ND | ND | 25 | ND | 25 | ND | ND | 25 | – |
| *Lactobacillus curvatus* | 5.0 | 22 | ND | ND | ND | 22 | ND | 22 | ND | ND | ND | – |
| *Pediococcus acidilactiei* | 5.0 | 40 | ND | ND | ND | 40 | ND | 40 | ND | ND | – | – |

[a]ND, not determined.
[b]–, ■■■■■■.
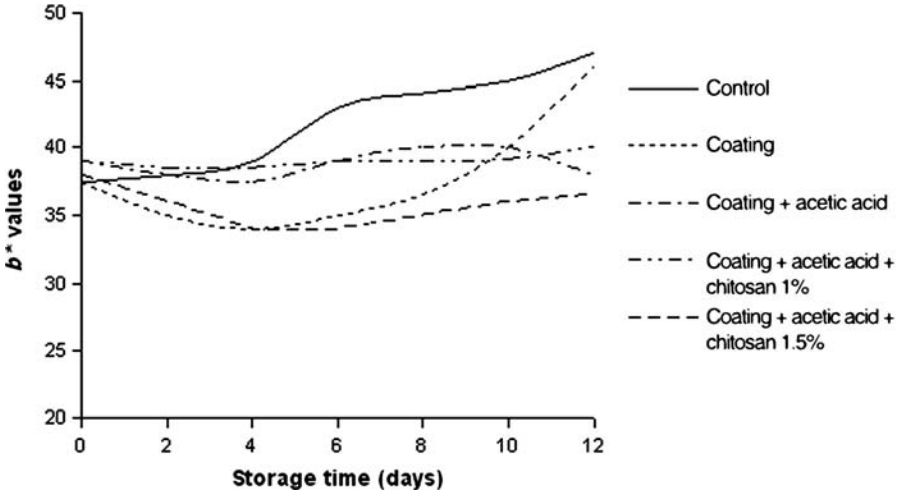
**Fig. 5-2** Skin color ($b^*$ values) of guava coated with starch/chitosan during 12 days of storage at room temperature.

and also reduces the loss of flavor and aroma. Fresh-cut vegetables and fruits lose their barrier (skin and peel), so that maintenance of the appropriate atmosphere for the product must be established by other means to maintain product shelf-life. Oxygen and $CO_2$ concentrations and also moisture loss must be taken into consideration. Interest in the quality and microbiological safety of minimally processed foods promotes the use of chitosan/starch coatings to preserve the products. Geraldine et al. (2007) showed significant inhibition of
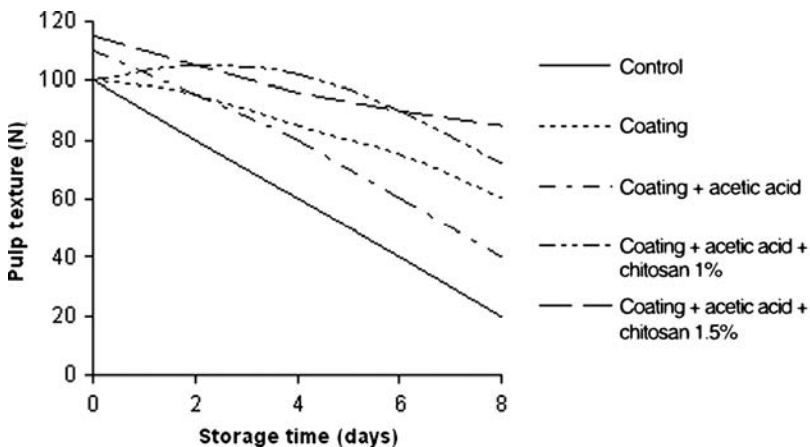


**Fig. 5-3** Pulp texture of guava coated with starch/chitosan during 12 days of storage at room temperature.
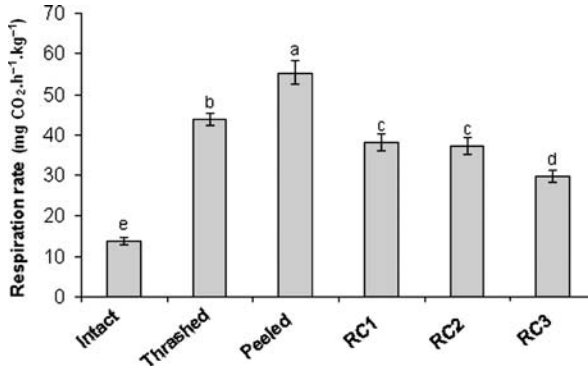
**Fig. 5-4** Garlic respiration rates at 25°C for different treatments: bulb (intact); cloves thrashed; cloves peeled; cloves peeled and coated with agar-agar (RC1), agar-agar and acetic acid (RC2), agar-agar, and chitosan (RC3). Bars represent the mean standard error. Means followed by the same letter were not significantly different ($P \geq 0.05$).
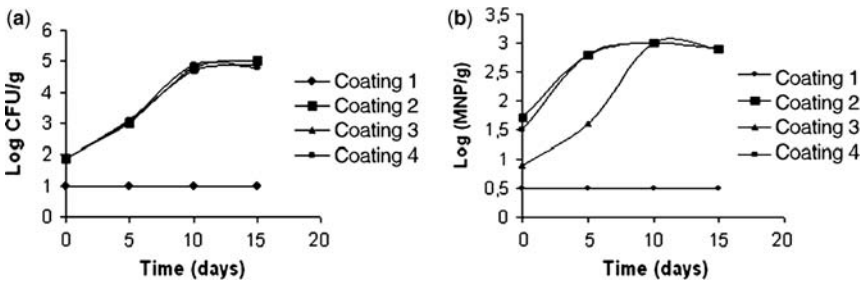


**Fig. 5-5** Effect of coatings on lactic acid bacteria (a) and total coliforms (b) in minimally processed carrot stored at 10°C for 15 days. Coatings are as defined in the text.
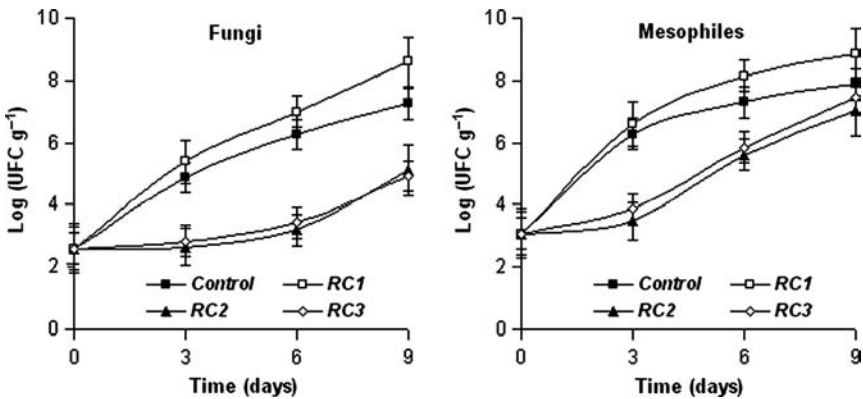


**Fig. 5-6** Filamentous fungi and yeasts and mesophilic aerobic counts of minimally processed garlic without coating (Control) and coated with agar-agar (RC1), agar-agar and acetic acid (RC2), and agar-agar and chitosan (RC3), during storage at 25°C. Bars represent mean and standard errors.
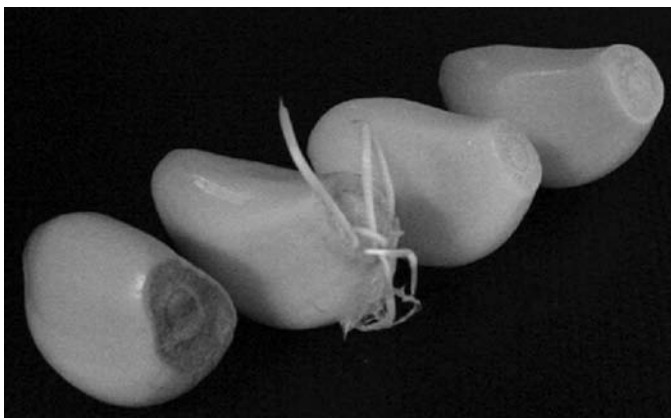
**Fig. 5-7** Left to right: Garlic cloves without coatings (control) and coated with agar-agar, agar-agar and acetic acid, and agar-agar and chitosan, after 9 days at 25°C.

growth of filamentous fungi and yeast and mesophiles on coated garlic cloves (see Fig. 5-6). Also, chitosan coatings affect root primordium formation and inhibit browning in garlic cloves (see Fig. 5-7).

## 5.5 OTHER PROPERTIES

Another important action attributed to chitosan is its antioxidant activity, which is dependent on molecular weight and concentration of chitosan. Kamil et al. (2002) investigated chitosan solutions of different viscosities (360, 57, and 14 cP; corresponding molecular weights of 1800, 960, and 660 kDa) with cooked, comminuted flesh of herring (*Clupea harengus*). The oxidative stability of fish flesh with added chitosans (50, 100, and 200 ppm) was compared with that with added conventional antioxidants, butylated hydroxyanisole + butylated hydroxytoluene (BHA + BHT, 200 ppm) and *tert*-butylhydroquinone (TBHQ, 200 ppm), during storage at 4°C. Among the three chitosans, 14 cP chitosan solution was most effective in preventing lipid oxidation evaluated by the formation of TBARS. At 200 ppm, 14 cP chitosan exerted an antioxidant effect similar to that of commercial antioxidants in reducing TBARS values in comminuted herring flesh. Similarly, Kim and Thomas (2007) also observed that the antioxidative effects of chitosan in salmon depended on its molecular weight (30, 90, and 120 kDa) and concentration (0.2%, 0.5%, and 1.0%). The 30 kDa chitosan showed higher scavenging activity than 90 and 120 kDa chitosan. The scavenging activities of chitosans increased with increasing concentration, except for the 120 kDa chitosan, which showed no significant difference with concentration.

Xue et al. (1998) suggested that the antioxidant mechanism of chitosan could be exerted by chelating action on metal ions and/or combination with lipids. Lipid

oxidation was evaluated on skinless pink salmon (*Oncorhynchus gorbuscha*) with an edible chitosan coating (Sathivel, 2005). After 3 months of frozen storage the chitosan coating was effective in reducing moisture loss of fillets by about 50% compared with the control uncoated fillets, and in delaying lipid oxidation. After the period of storage, the edible coating showed no effect on whiteness values for cooked pink salmon fillets. In another study with cod patties the chitosan coating was effective as a protective film, retarding lipid oxidation and microbial spoilage, and acted as a barrier against oxygen (Jeon et al., 2002).

In many countries sodium nitrite is used as a curing agent for color and flavor development as well as preservative effect in various meat products. However, nitrite reacts with amines in meat and may produce nitrosoamine, a strong toxicant detrimental to human health. Some workers (Park et al., 1999; Youn et al., 1999, 2001) have investigated the possible role of chitosan in lieu of sodium nitrite as curing agent in sausages, and found that addition of chitosan could reduce or replace the use of nitrite without affecting preservative effect and color development. A mixture of 0.2% chitosan (120 kDa, DD = 85%, dissolved in 0.3% lactic acid) and 0.005% sodium nitrite or 0.5% chitosan alone exhibited the same preservative effect as did 0.01% sodium nitrite alone when added in meat sausage. The addition of 0.2% chitosan (30 kDa, DD = 92%) dissolved in 0.3% lactic acid reduced sodium nitrite by half of the standard amount (150 ppm) without affecting the quality and storage stability of sausage. In addition to the preservative effect, chitosan also notably reduced the concentration of residual nitrite in sausage. The concentration of residual nitrite in sausage decreased with increasing molecular weight and concentration of chitosan.

Geraldine (2004) evaluated the thermal treatment (121°C for 15 min) of chitosan solution (1% chitosan – 1% acetic acid), for the preparation of a coating solution (0.24% chitosan) and reported a low effect on antifungal activity (*Aspergillus niger*). In the same study the author also investigated the effect of chitosan and acetic acid concentration on colony diameter and germination of *A. flavus* (see Table 5-2). The fungus sporulated but showed no growth in the culture medium.

## 5.6  CHITOSAN DERIVATIVES

After chitosan, the most studied derivative of chitin is carboxymethylchitin (CM-chitin), a water-soluble anionic polymer. The carboxymethylation of chitin is done similarly to that of cellulose; chitin is treated with monochloroacetic acid in the presence of concentrated sodium hydroxide (Rindlav-Westling et al., 1998). The method for cellulose derivatization is also used to prepare hydroxypropylchitin, a water-soluble derivative used for artificial lachrymal drops (Rico-Peña and Torres, 1990; Rindlav-Westling et al., 1998). Other derivatives such as fluorinated chitin (Robertson, 1993), *O*-sulfated chitin (Redl et al., 1996; Sotero, 2000; Sebti and Coma, 2002), (diethylamino)ethylchitin (Sothornvit and Krochta, 2001), phosphoryl-chitin (Stuchell and Krochta, 1995), mercaptochitin (Tatsumi et al., 1991), and chitin carbamates (Tharanathan and Farooqahmed, 2003) have been described in the

**TABLE 5-2  Effect on the Growth of A. _niger_ of the Increase of Acetic Acid in 1% Agar-Agar Solution Incorporating 0.36% Chitosan**

| Chitosan Content | Parameter | Concentration of Acetic Acid (%) | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | | 0.12 | 0.13 | 0.14 | 0.15 | 0.16 |
| Without chitosan | pH | 3.63 | 3.60 | 3.57 | 3.55 | 3.53 |
| | Diameter (mm)[a,b] | $13.97 \pm 1.42^a$ | $11.91 \pm 1.12^{ab}$ | $10.29 \pm 0.84^b$ | $7.82 \pm 0.45^c$ | $0^d$ |
| | Germination | + | + | + | + | – |
| With chitosan (0.36%) | pH | 5.00 | 4.93 | 4.87 | 4.82 | 4.78 |
| | Diameter (mm) | 0 | 0 | 0 | 0 | 0 |
| | Germination | + | + | + | + | + |

[a]Values are mean $\pm$ standard error.
[b]Means followed by the same superscript letter within the row are not significantly different by the Tukey test ($P \geq 0.05$).

literature. Modification of chitin is also often effected via water-soluble derivatives of chitin (mainly CM-chitin).

The same type of chemical modifications (etherification and esterification) as for cellulose can be performed on the available C-6 and C-3 hydroxyl groups of chitin (Prashanth and Tharanathan, 2007). Chitin can be used in blends with natural or synthetic polymers; it can be crosslinked by the agents used for cellulose (epichlorhydrin, glutaraldehyde, etc.) or grafted in the presence of ceric salt (Prashanth and Tharanathan, 2007) or after selective modification (Williams et al., 1978). Chitin is partially degraded by acid to obtain series of oligochitins (Lerdthanangkul and Krochta, 1996; Wong et al., 1994). These oligomers, as well as those derived from chitosan, are recognized for their bioactivity, including antitumor, bactericidal, and fungicidal activity, eliciting chitinase and regulating plant growth. They are used in testing for lysozyme activity and are also used as active starting blocks to be grafted onto protein and lipids to obtain analogues of glycoproteins and glycolipids.

To enhance the antibacterial potency of chitosan, thiourea chitosan was prepared by reacting chitosan with ammonium thiocyanate followed by its complexation with silver (Chen et al., 2005). It has been reported that quaternary ammonium salts of chitosan exhibit good antibacterial activities; for example, diethylmethyl chitosan chloride showed higher antibacterial activity than chitosan.

With the same aim of improving antibacterial activity, Xie et al. (2007) reported novel synthetic procedures for the preparation of chitosan derivatives with a quaternary ammonium salt, expecting to improve its water solubility and anti-bacterial activity. The quaternary derivative (ethylamine hydroxyethyl chitosan [EHC]) was prepared by treating hydroxyethyl chitosan (HEC) with chloro-ethylamine hydrochloride in sodium hydroxide solution. This work suggested that EHC decreased the intermolecular interactions, such as van der Waals forces, and increased water solubility. Derivates showed good inhibitory effects against *Escherichia coli*, and $NH_2\%$ was the factor that most strongly affected the anti-bacterial activity.

Novel *N,O*-acylchitosan derivatives were more active than chitosan itself against the gray mould fungus *Botrytis cinerea* and the rice leaf blast fungus *Pyricularia oryzae*, and the effect was concentration dependent (Badawy et al., 2004). Hydroxypropyl chitosan grafted with maleic acid sodium killed over 99% of *Staphylococcus aureus* and *E. coli* within 30 min of contact at a concentration of 100 ng/ml. It was a potent inhibitor of *Azotobacter mali*, *Clostridium diplodiella*, *Fusarium oxysporum*, and *Pyricularia piricola*. The degree of hydroxypropyl group substitution also influenced the antifungal activity. With regard to their antifungal mechanisms, it was reported that these chitosan derivatives directly interfered with fungal growth and activated several defense processes, such as accumulation of chitinases, synthesis of proteinase inhibitors and induction of callous synthesis. It was also noted that the antibacterial activity of chitosan derivatives increased with increasing chain length of the alkyl substituent, and this was attributed to the increased hydrophobicity (Prashanth and Tharanathan, 2007).

Some applications for food coating or film require better controlled release of the incorporated components, such as additives, antioxidants, and aromas from the film/coating into the packed food. To enhance this property, nanocomponents has been added to chitosan-based films and coatings. Chitosan/organic rectorite (chitosan/OREC) nanocomposite films with different mass ratios of chitosan to organic rectorite and corresponding drug-loaded films were obtained by a casting/solvent evaporation method. Rectorite is a kind of layered silicate, with structure and characteristics much like those of montmorillonite. The addition of OREC to pure chitosan film influenced many of the properties. The enhancement of properties was related to the amount and the interlayer distance of the layered silicate in the chitosan/OREC nanocomposite films. In-vitro studies of controlled drug release showed a slower and more continuous release from the nanocomposite films than from pure chitosan film. Chitosan/OREC nanocomposite films provide promise as applications as antimicrobial agents, water-barrier compounds, antiultraviolet compounds, and controlled drug release carriers in antimicrobial food packaging and drug-delivery system (Wang et al., 2007).

Copolymer hydrogels have similarly been studied for control of compound delivery. These thermosensitive hydrogels, which are triggered by changes in environmental temperature to give in-situ hydrogel formation, have recently attracted the attention of many investigators for biomedical applications. Tang et al. (2007) aimed to develop an injectable and thermosensitive system based upon a blend of chitosan and poly(vinyl alcohol) (PVA) that can serve as a therapeutic drug-delivery system promoting tissue repair and regeneration through controlled release of loaded drugs. The thermosensitive hydrogel was prepared by mixing chitosan, PVA, and sodium hydrogencarbonate. The mixture was a liquid aqueous solution at low temperature (about 4°C) but a gel under physiological conditions, at which bioactive species can be safely and uniformly incorporated. These copolymer hydrogels are potentially suited for a wide range of in-vivo biomedical applications, such as drug release and tissue repair and regeneration. The system has been tested for drug delivery but it can also be applied for release of food additives.

The presence of *N*-sulfofurfuryl and quaternary ammonium groups has a remarkable impact on the response of the chitosan film to charged proteins in terms of adsorbed quantity and selectivity.

Taking advantage of the availability of functional groups for chemical reactions at the chitosan surface and the diverse bioactivity of its charged derivatives, Hoven et al. (2007) aimed to tailor protein adsorption at the chitosan surface by chemically introducing charged functionalities specifically to amino groups under heterogeneous conditions. The charged-modified chitosan surfaces are exposed to proteins having different molecular weights and isoelectric points. Besides hydrophobic interactions and hydrogen bonding, it is hypothesized that the extent of protein adsorption should depend also on electrostatic interaction between protein molecules and the modified groups on the chitosan surface. This surface modification should expand the applicability of chitosan in biomedical-related fields.

Positive and negative charges were introduced to chitosan surfaces via methylation using methyl iodide (MeI) and reductive alkylation using 5-formyl-2-furan sulfonic acid (FFSA). The chitosan films bearing negative charges of *N*-sulfofurfuryl groups on their surface (SFC films) exhibited selective protein adsorption against both negatively charged proteins (albumin and fibrinogen) and positively charged proteins (ribonuclease, lysozyme). The adsorption can be explained in terms of electrostatic attraction and repulsion. In contrast, the adsorption behavior of chitosan films bearing positive charges of quaternary ammonium groups on their surface (QAC films) was anomalous. The quantity of the adsorbed protein tended to increase as a function of the swelling ratio of the QAC films regardless of the charge characteristics of the protein. The ability to sustain their charges in a broader pH range should make these surface-charged chitosan films more versatile in applications than native chitosan films for which the charge is altered as a function of environmental pH (Jia et al., 2001).

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# Blends and Composites Based on Cellulose and Natural Polymers

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## 6.1 INTRODUCTION

In the twenty-first century, science and technology have moved toward renewable raw materials and more environmentally friendly and sustainable resources and processes (Schurz, 1999). The Technology Road Map sponsored by the US Department of Energy (DOE) has targeted the achievement of 10% of basic chemical building blocks arising from plant-derived renewable sources by 2020 (Mohanty et al., 2002). Natural polymers from plants, such as cellulose, starch, and protein, have been reevaluated not only as sustainable resources but also as fascinating safer

chemicals with various uses as materials. The research and development of natural polymers is an ancient science, and it now attracts much attention for preparation of materials with new functions by the use of powerful modern tools. Renewable resource (RR) is a modern term for an old subject; it arose between 1973 and 1979 when the price of crude oil was lifted. RRs are products originating from plants and animals and used for industrial purposes; these also include food products that are not used for nutrition, as well as wastes and co-products of food processing (Zoebelein, 2001). Table 6-1 lists some natural polymers (Yu et al., 2006). However, one of the main disadvantages of biodegradable polymers obtained from RRs limits their applications; this involves their dominant hydrophilic character, fast degradation rate, and, in some cases, unsatisfactory mechanical properties, particularly under wet conditions (Yu et al., 2006). Thus, the research into and applications of natural polymers are focused on chemical and physical modifications to improve their mechanical properties, water resistance, and flexibility. Novel biodegradable materials can be obtained by blending cellulose and its derivatives with other natural polymers, and these products have promising applications in a number of fields.

Cellulose is one of the oldest and most abundant natural polymers. It is renewable, biodegradable, biocompatible, and derivatizable, and it possesses several further advantages such as low density, high modulus and high strength, high stiffness, little damage during processing, few requirements on processing equipment, and relatively low price (Zadorecki and Michell, 1989; Joly et al., 1996). As a chemical raw material, cellulose has been used for more than 150 years, and is considered an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products (Klemm et al., 2002). However, the full potential of cellulose has not yet been exploited because of the lack of environmentally friendly methods and the limited number of common solvents that readily dissolve cellulose (Zhu et al., 2006). The traditional cuprammonium and xanthate processes are often cumbersome or expensive and require the use of unusual solvents, typically with high ionic strength, and use relatively harsh conditions (Heinze and Liebert, 2001; Zhu et al., 2006). It is notable that the traditional viscose route for producing

**TABLE 6-1    List of Natural Polymers (Kalplan DL, 1998)**

| *Polysaccharides* | |
| --- | --- |
| Plant/algal | Starch, cellulose, pectin, konjac, alginate, carageenan, gums |
| Animal | Hyluronic acid |
| Fungal | Pulluan, elsinan, scleroglucan |
| Bacterial | Chitin, chitosan, levan, xanthan, polygalactosamine, curdlan, gellan, dextran |
| *Proteins* | Soy, zein, wheat gluten, casein, serum, albumin, collagen/gelatin, silks, polylysine, polyamino acids, poly($\gamma$-glutamic acid), elastin, polyarginyl-polyaspartic acid |
| *Lipids/surfactants* | Acetoglycerides, waxes, surfactants, emulsan |
| *Speciality polymers* | Lignin, shellac, natural rubber |

regenerated cellulose fibers, films, and nonwoven fabrics still dominates the current processing route (Klemm et al., 2005). Carbon disulfide ($CS_2$), a toxic gas, has been used to prepare cellulose products in the viscose process, but this can enter the human body through the breath, skin, and digestive tract, leading to the destabilization of protein. Moreover, waste containing $CS_2$ and hydrogen sulfide ($H_2S$) will rot the roots of plants and destroy the equilibrium of the soil. There is therefore a growing urgency to develop novel nonpolluting processes for fiber production in the cellulose industries to meet environmental concerns. Recently, the new and powerful organic solvent N-methylmorpholine-N-oxide (NMMO), has been developed and used for preparing regenerated cellulose films and fibers (Schurz, 1999; Fink et al., 2001). Ionic liquids are a group of new organic salts that are termed "green" solvents of cellulose (Swatloski et al., 2002; Turner et al., 2004; Zhang H et al., 2005; Abbott et al., 2006; Zhu et al., 2006). Rogers RD was a winner of the 2005 US Presidential Green Chemistry Challenge Awards (United Environmental Protection Agency, EPA744-K-05-001) for his great contribution to the dissolution of cellulose in ionic liquids and its regeneration (Zhu et al., 2006). We have recently developed new types of solvent mixtures for cellulose/NaOH/urea, NaOH/thiourea, and LiOH/urea aqueous solutions, precooled to low temperatures (between $-5$ and $-12°C$)—in which cellulose can be dissolved rapidly to obtain a transparent cellulose solution (Cai and Zhang, 2006; Cai et al., 2006; Ruan et al., 2006). Moreover, we have successfully produced multifilament fibers from cellulose solutions in the NaOH/urea and NaOH/thiourea aqueous systems with pilot machinery (Ruan et al., 2006; Cai et al., 2007a). Unsurprisingly, regenerated cellulose films and fibers prepared from "green" process have attracted much attention because of their great potential for sustainable development.

It is well known that polymer/polymer blending is an effective method for improving the original physical properties of one or both of the components, or for preparing new polymeric materials that exhibit widely variable properties without parallel in homopolymers (Nishio, 2006). Usually, two basic means are used to make a blend: mixing the components in the softened or molten state, and blending of components from their solutions. A great deal of attention has been paid to composites based on cellulose and other natural polymers, which are totally environmentally friendly and can be considered substitutes for the polymers obtained from petroleum. However, cellulose has poor solubility in organic solvents and has a low thermal decomposition temperature, which lies below its melting point. These properties make it difficult to disperse cellulose in melted polymers and a suitable solvent system is urgently required. Usually, chemical modification is used to prepare cellulose derivatives, and these are then blended with other natural polymers to produce new materials. Meanwhile, with the great efforts put into solvent systems for cellulose, a series of cellulose/natural polymer blends have been successfully obtained. In this chapter, an attempt is made to review the state of the art of composites of cellulose blended with chitin, chitosan, alginate, protein, and konjac glucomannan over past decade. Blends containing cellulose derivatives (cellulose esters and ethers) and natural polymers are also discussed.

## 6.2 CELLULOSE: STRUCTURE AND SOLVENTS

### 6.2.1 Structure of Cellulose

In 1838 the French chemist Anselme Payen (1795–1871) produced a resistant fibrous compound by treating various plant tissues alternately with nitric acid and sodium hydroxide (NaOH) solutions; this plant constituent was named "cellulose" in 1839 (Heuser, 1944). Cellulose is a polydisperse, linear-chain carbohydrate homopolymer, that is generated from repeating cellobiose units covalently linked through acetal functions between the OH group of the C4 and the C1 carbon atoms (β-1, 4-glucan). There is a large number of hydroxyl groups in the cellulose, and they are placed at positions C2 and C3 (secondary, equatorial) as well as C6 (primary) in a β-1,4-D-glucan unit, in general accessible to the typical conversions of primary and secondary alcoholic OH groups. These three different OH groups are considered to be an important factor influencing the physical properties of cellulose; they react easily with various reagents, allowing the synthesis of derivatives (Cazacu and Popa, 2005). The cellulose chain consists at one end of a D-glucose unit with an original C4-OH group (the nonreducing end); the other end is terminated with an original C1-OH group, which is in equilibrium with the aldehyde structure (the reducing end) (Klemm et al., 2005). The molecular structure of cellulose is shown in Fig. 6-1 (Heinze and Liebert, 2001). Its molecular formula is determined to be $C_6H_{10}O_5$, and the anhydroglucose unit (AGU) presents a $^4C_1$ conformation (Nehls et al., 1994).

### 6.2.2 Solvents of Cellulose

Cellulose is difficult to process in solution or as a melt because of the large numbers of intra- and intermolecular hydrogen bonds in cellulose, which form a highly organized network system surrounding the single polyglucan chain and interrupt the dissolution of cellulose solid into solution. Thus the key to the application of cellulose is to search for a solvent that can effectively destroy the intra- and interchain hydrogen bonding in cellulose. A nontoxic and easy dissolution system for cellulose has been developed, and it includes indirect and direct solvent systems. In indirect solvent systems, such as dimethylformamide/pyridine, dimethylformamide/$N_2O_4$, and dimethyl sulfoxide/$N_2O_4$, cellulose forms derivatives during dissolution. Direct solvent systems such as trifluoroacetic acid/dichloromethane, liquid ammonia/$NH_4SCN$, dimethylacetamide/LiCl, and NMMO/$H_2O$ may form complexes with
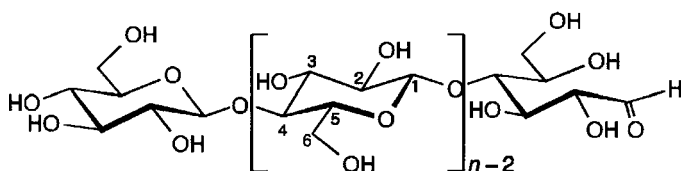


**Fig. 6-1** Molecular structure of cellulose including numbering of carbon atoms ($n = $ DP, degree of polymerization) (Heinze and Liebert, 2001).

cellulose, but the molecular structure of cellulose is not altered (Kim et al., 1999). A suitable classification of cellulose solvents identifies five types of systems as follows.

***NMMO Solvent System*** The most advanced development took place in the 1980s with a process based on the *N*-methylmorpholine-*N*-oxide (NMMO) monohydrate solvent system (Firgo et al., 1995). Owing to its strong N—O dipole, NMMO in combination with water can dissolve cellulose typically as the monohydrate (about 13% water) at about 100°C (Michael et al., 2000) without prior activation or derivatization. Furthermore, solutions with high cellulose content of up to 23% can be produced by dispersing conventional cellulose into NMMO with high water content (such as 50%) and then subsequently removing water with an applied vacuum until the dissolution of the cellulose. This novel, environmentally friendly, direct solvent system leads to a new class of man-made cellulose fibers with the generic name of Lyocell (Woodings, 2001). Lyocell fibers show better performance qualities, but the Lyocell process suffers from uncontrolled thermal stability of the NMMO/ cellulose/$H_2O$ system (a runaway reaction), high evaporation costs (energy costs), and high tendency to fibrillation of the Lyocell fiber (Fink et al., 2001), which limit the enlargement of production. Meanwhile, the solvent systems NMMO/ $H_2O$/DMSO (Chanzy et al., 1979) and NMMO/$H_2O$/DETA (Drechsler et al., 2000) have proved to be thermodynamically good solvents for cellulose and suitable for samples of various origins. A solution of 32.6 wt% NMMO, 10.0 wt% $H_2O$, and 57.4 wt% DETA can dissolve cellulose at room temperature, and a slightly elevated temperature (40°C) at the beginning of the dissolution process will lead to considerable shorter dissolution time (Heinze and Liebert, 2001).

***LiCl/DMAc Solvent System*** Around 1980 it was discovered that *N,N*-dimethylacetamide (DMAc) containing lithium chloride (~8–9 wt%) can dissolve cellulose (McCormick, 1981; Turbak et al., 1981). This system shows enormous potential for cellulose in organic syntheses (Dawsey and McCormick, 1990) as well as for analytical purposes (Burchard et al., 1994) because the solvent is colorless and dissolution succeeds without or at least with negligible degradation even in the case of high molecular weight polysaccharides such as cotton linters or bacterial cellulose (Heinze and Liebert, 2001). The content of cellulose in solution can reach to 15 wt%, while that of LiCl is 5–9 wt% after dissolution for 6 h at 100°C (Conio et al., 1984). Cellulose of high molecular weight can be dissolved and the dissolution time can be shortened if the start temperature of the dissolution process is 150°C and the system is cooled slowly. Empirically determined solvatochromic polarity parameters for the cellulose/LiCl/DMAc system indicate that the ability to keep cellulose in solution is due to the very strong chloride–cellulose interaction. The chloride–cellulose interaction contributes about 80% to the dipolar–dipolar interactions between DMAc and cellulose, whereas the specific $Li^+(DMAc)_n$–cellulose interaction contributes about 10% (Spange et al., 1998).

***Aqueous Metal-Based Solvent System*** Aqueous solutions of a number of metal complexes have been found to dissolve cellulose. The best known solvent of

this group is cupric hydroxide in aqueous ammonia, which is often called cuoxam. Cellulose can be dissolved to a molecular level in cuoxam, and most effective is coordinative binding of the metal complex to the deprotonated hydroxyl groups in the C2 and C3 positions of the AGU in the chain (Fuchs et al., 1993; Burchard et al., 1994). However, cuoxam has some disadvantages, which consist of easy degradation of the cellulose chain, a deep blue color, and a restricted dissolution power that is limited to degrees of polymerization of $DP_w < 5000$. Metal ions such as $Cu^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Fe^{2+}$, and $Co^{2+}$ have been used to form complexes with ethylenediamine (en) and other polydentate ligands and all these reagents gave clear solutions, indicating full solubility of the cellulose. A number of modern aqueous metal complex solvents, such as aqueous solutions of Ni-tren and Cd-tren (tren = tris(2-aminoethyl)amine), have been produced, and the dissolution of a large number of samples, cotton linters, various pulp celluloses, and bacterial celluloses has been studied. Both these solvents exhibited good solution properties, but only Cd-tren was capable of dissolving cotton linters and bacterial cellulose of the highest degrees of polymerization ($DP_w = 9700$) (Saalwächter et al., 2000).

***Ionic Liquid Solvent System*** Room-temperature ionic liquids (ILs) have recently received significant attention due to their favorable of properties including low melting points, wide liquid ranges, and lack of vapor pressure, which have encouraged researchers to explore known chemical reactions and processes in place of volatile organic solvents (Turner et al., 2004; Heinze et al., 2005). The IL 1-butyl-3-methylimidazolium chloride (BMIMCl) can be used as a nonderivatizing solvent for cellulose. It has been shown that ILs incorporating anions that are strong hydrogen bond acceptors are most effective, especially when combined with microwave heating, whereas ILs containing "noncoordinating" anions, including $(BF_4)^-$ and $(PF_6)^-$ are nonsolvents. Chloride-containing ILs appear to be the most effective solvents, presumably solubilizing cellulose through hydrogen-bonding from hydroxyl functions to the anions of the solvent (Swatloski et al., 2002). More recently, a novel IL, 1-allyl-3-methylimidazolium chloride (AMIMCl) has been used to carry out homogeneous esterification of cellulose (Wu J et al., 2004; Zhang et al., 2005).

***NaOH/Urea Aqueous Solvent System*** A novel solvent system that has been developed for cellulose is a NaOH/urea aqueous solution precooled to $-12°C$. Dissolution of cellulose could be achieved rapidly (about 5 min) at ambient temperatures (below 20°C), and the resulting solution is colorless and transparent (Zhang L et al., 2001, 2005). Interestingly, cellulose with a relatively high molecular weight could not be dissolved in the solvent without being precooled to $-12°C$ or without urea being added. The result from $^{13}C$ NMR indicated that this system is a good direct solvent of cellulose with nonderivatizing processes (Cai and Zhang, 2005). The addition of urea and the low temperature play important roles in the improvement of cellulose dissolution because low temperature creates a large and stable inclusion complex associated with cellulose, NaOH, urea, and $H_2O$ clusters through hydrogen-bonding, which destroys effectively the interchain

hydrogen bonding in cellulose and bring cellulose into aqueous solution. Multifilament fibers have been produced successfully from the cellulose dope using a pilot machine (Cai et al., 2007a). The cellulose dope could remain in a liquid state for a long period (more than a week) at about 0–5°C (Cai and Zhang, 2006). This solvent system has been shown to be an economical and environmentally friendly cellulose-fiber fabrication process on an industrial scale. In addition, NaOH/thiourea (Ruan et al., 2004, 2006) and LiOH/urea (Cai et al., 2007a, b) aqueous systems have been used to rapidly dissolve cellulose, and these exhibit greater solubility for cellulose than NaOH/urea.

## 6.3   CELLULOSE/NATURAL POLYMER BLENDS

### 6.3.1   Cellulose/Chitin and Cellulose/Chitosan Blends

Chitin, a polymer composed of $N$-acetyl-D-glucosamine residues that is extracted from crab and shrimp shells, is the second most abundant resource (next to cellulose) in nature (Parisher and Lombardi, 1989); chitosan is obtained by $N$-deacetylation of chitin. Both chitin and chitosan have good biocompatibility (Shigemasa and Minami, 1995) and biodegradability (Shigemasa and Minami, 1995), along with various biofunctionalities including antithrombogenic, homeostatic, immunity enhancing and wound healing (Hirano, 1996; Muzzarelli, 1997), and they are recognized as excellent metal ligands, forming stable complexes with many metal ions (Chui et al., 1996). The similarity in chemical structure of cellulose, chitin, and chitosan fundamentally determines their compatibility and makes it possible to prepare homogeneous blends combining the unique properties of chitin and chitosan with the availability of cellulose (Rogovina et al., 2006). Due to the high adhesiveness between them (Isogai et al., 1992), addition of even relatively low amounts of chitin or chitosan to cellulose-based products allows significant increases in their mechanical strength, bactericidal properties, and other characteristics (Yunlin et al., 1998).

**Reinforced Materials**   Cellulose and chitin are polymers that show miscibility in the solid state. Fibers made from cellulose and chitin in various proportions have been wet spun from their solutions in dimethylacetamide containing 5 wt% LiCl (Marsano et al., 2002). Polymer concentration was purposely maintained as low as possible (2.4 wt%) and the dope temperature was 60°C to have give spinability. The mechanical behaviors of blends highlighted a synergistic interaction between the components. Thus, the elastic modulus ($E$) of fibers increased when chitin was added to cellulose dope and vice versa, reaching the maximum value of 15 GPa at a cellulose/chitin ratio of about 1/1 w/w, while the values for neat cellulose and chitin fibers were 9 and 11 GPa, respectively. Application of a pull-off ratio during the coagulation allowed the $E$ value to be increased further. These results, as well as electron microscopy of the fiber sections, concur with complete miscibility of two polymers in the solid state, and it is believed that the DMAc/LiCl system can induce a high degree of interaction between chitin and cellulose and a consequent physical

network able to be stretched and to realize a high molecular orientation level inside the cellulose/chitin fibers.

A 6 wt% NaOH/4 wt% urea aqueous solution (Zhang L et al., 2000a; Zhou and Zhang, 2000) and a 1.5 M NaOH/0.65 M thiourea aqueous solution (Zhang L et al., 2000; Zhang et al., 2002) have been used to prepare regenerated cellulose/chitin blend films (RCCH) (Zhang L et al., 2002a; Zheng et al., 2002b). The cellulose/chitin blends exhibit a moderate miscibility, and achieved maximum tensile strength in dry and wet states of 89.1 and 43.7 MPa, respectively, when the chitin content was 10 wt%. The tensile strength ($\sigma_b$) and water resistivity of the RCCH film are higher than those of the regenerated cellulose (RC) film unblended with chitin. In addition, compared to the mechanical properties of chitin film, those of the RCCH films containing 10–50 wt% chitins are significantly improved (Zheng et al., 2002). Two coagulation systems have been used to prepare cellulose–chitin blend films; one is 5 wt% $H_2SO_4$ (system H), and the other is 5 wt% $CaCl_2$ followed by 5 wt% $H_2SO_4$ (system C) (Zhang et al., 2002a). The system H blend membranes have relatively dense structure, high crystallinity, and strong intermolecular hydrogen bonding between cellulose and chitin, leading to higher mechanical properties and thermal stability. When the chitin content is 7.5 wt%, the $\sigma_b$ value of the blend membrane is 90.4 MPa and even higher than that of the system H unblended RC membrane, and the values of $\varepsilon_b$ for the blend membranes H and C are all higher than unblended membranes H-RC and C-RC, respectively. This provides promising application in the pharmaceutical and biomedical fields for chitin in functional materials retaining its characteristics. The blend membranes C had a mesh structure and relatively large pores ($2r_e = 210\ \mu m$) due to a loss of chitin in the process, resulting in lower $\sigma_b$ and higher $\varepsilon_b$. The intermolecular hydrogen bonds between the cellulose and the chitin in the blends can be broken in 5 wt% $CaCl_2$ aqueous solution, in which a water-soluble calcium complex of chitin as pore former is removed from membranes.

***Antibacterial Materials***    A solution of a blend of cellulose xanthate with chitin xanthate has been successfully prepared, and fibers were subsequently wet spun from this solution (Pang et al., 2003). According to the bacteriostatic test GB15981–1995 I Pasteurization and Supervision Technical Standard of Pasteurization Product, both the blend fibers and the woven fabric made from the blend fibers after processing and several machine washings contained 3.54 wt% chitin and have an effective bacteriostatic effect >26% on *Staphylococcus aureus*, *Escherichia coli*, and *Corynebacterium michiganense*. Chitosan is known to be able to accelerate the healing of wound in humans (Cho et al., 1999; Ueno et al., 1999). Chitosan shows considerable antibacterial activity against a broad spectrum of bacteria (Muzzarelli et al., 1990). Polysaccharide-based membranes of chitosan and cellulose blends have been prepared using trifluoroacetic acid as a cosolvent (Wu YB et al., 2004). The intermolecular hydrogen bonding of cellulose is supposed to break down to form cellulose–chitosan hydrogen bonding; however, the intramolecular and intrastrand hydrogen bonds hold the network flat. The reduced water vapor transpiration rate through the chitosan/cellulose membranes indicates that the membranes used
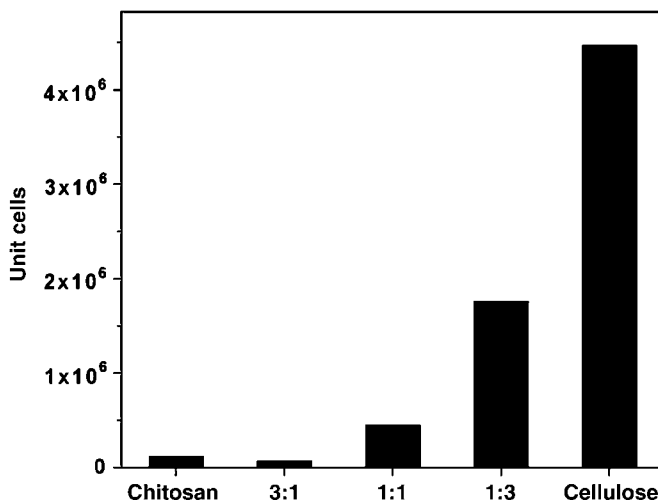
**Fig. 6-2** Bacteriostatic effect of cellulose, chitosan, and chitosan/cellulose blends on the growth of *Escherichia coli* (Wu YB et al., 2004).

as wound dressings may prevent excessive dehydration of the wound. In addition, chitosan/cellulose blend membranes exhibited effective antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus*, shown in Fig. 6-2. Thus, chitosan/cellulose blend membranes may be suitable for use as wound dressings with antibacterial properties.

The introduction of —CH$_3$COO— groups into the —OH of chitosan can give an improved antibacterial activity (Liu XF et al., 2001). Two types of *O*-carboxymethylated chitosan (*O*-CMCh)/cellulose polyblends have been prepared by mixing cellulose in LiCl/DMAc solution with *O*-CMCh aqueous solution or DMAc emulsion, and their corresponding films were regenerated in water (Li et al., 2002). FT-IR analyses showed that amino groups of *O*-CMCh were not affected during the film formation, and that there was some interaction between *O*-CMCh and cellulose in the blends, improving their compatibility. From the results of SEM observations, the *O*-CMCh/cellulose polyblend displays a heterogeneous microstructure. *O*-CMCh microdomains disperse in the cellulose matrix of the blend film. The addition of *O*-CMCh did not significantly influence the crystallinity and thermal properties. The antibacterial activity of the films against *Escherichia coli* was also measured by an optical density method. Both blend films exhibited satisfying antibacterial activity against *E. coli*, even at *O*-CMCh concentration of only 2 wt%. Due to the coagulation effect of water on the polyblend, *O*-CMCh water solution is suitable for the preparation of the low *O*-CMCh-content blend film, while *O*-CMCh/DMAc emulsion is used for high *O*-CMCh-concentration blends.

***Sorption Active Materials*** Cellulose/chitin beads prepared in 6 wt% NaOH−5 wt% thiourea aqueous solution by coagulating with 5 wt% H$_2$SO$_4$ have been found to

be an effective biosorbent for the removal of heavy metals such as $Pb^{2+}$, $Cd^{2+}$, and $Cu^{2+}$ (Zhou et al., 2004a). Interestingly, the sorption activity for cellulose–chitin on heavy metals is significantly higher than that of both pure cellulose and chitin beads. The beads exhibit microporous structure (shown in Fig. 6-3), large surface area, and high affinity for metals. The uptakes of $Pb^{2+}$, $Cd^{2+}$, and $Cu^{2+}$ ions on cellulose/chitin beads are 0.33 mmol/g at pH 4, 0.32 mmol/g at pH 5, and 0.30 mmol/g at pH 4, respectively.

The adsorption equilibrium is well described by the Langmuir adsorption isotherm, which is valid for monolayer adsorption onto a surface with a finite number of identical sites. The temperature and ionic strength of the solution did not exhibit a significant effect on the amount of metal ions adsorbed over the tested temperature range of $10–40°C$. This suggests that chemisorption mechanisms play the controlling part in the adsorption. The adsorption of these heavy metals is selective in the order $Pb^{2+} > Cd^{2+} > Cu^{2+}$ in solution of low ionic concentration. Adsorption equilibrium was established within 4–5 h for these ions on beads. However, the cellulose/chitin beads can easily be regenerated within 5–10 min using 1 mol/l HCl with up to 98% recovery. The adsorption mechanisms of heavy metals by cellulose/chitin beads mainly involve complexation between heavy metal ions and chitin at low pH as well as hydrolysis adsorption and surface microprecipitation at high pH. In addition, the network structure and hydrophilic skeleton of the cellulose/chitin beads could promote adsorption. Further research on the ability of these beads to adsorb $Pb^{2+}$ in aqueous solution has been done with a fixed-bed column (Zhou et al., 2004b). The resulting breakthrough curves for the adsorption behavior indicated that the column performance is improved with decreasing initial lead concentration, ionic
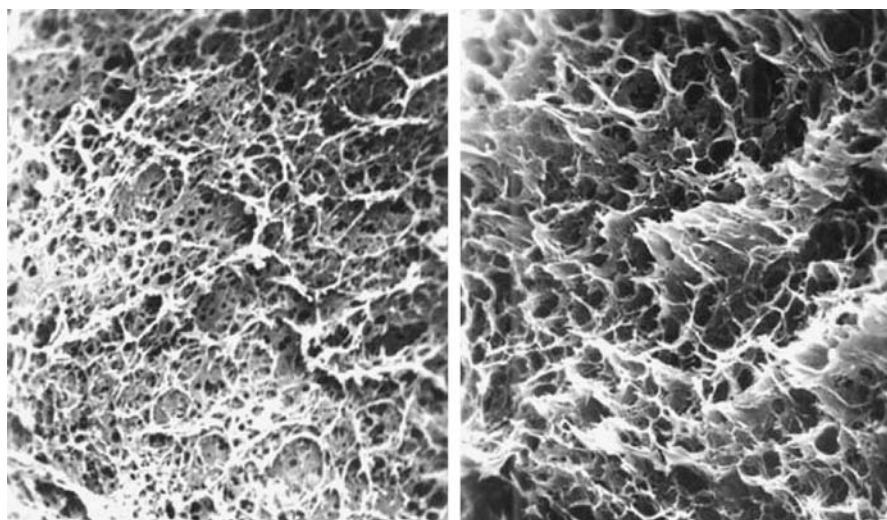


**Fig. 6-3**    SEM of surface (left) and cross-section (right) of cellulose/chitin beads (Zhou et al., 2004a).

strength, flow velocity, or bead size, as well as increasing pH and bed height. It is notable that the efficiency of the column for the removal of lead is not significantly reduced (by not more than 5%) after four adsorption–desorption cycles. Preparation of cellulose/chitin beads is simple and low cost; they have potential application in industrial wastewater treatment for removal and recovery of heavy metals; and the materials are biodegradable after use, giving favorable environmental credentials.

Cellulose/chitosan blends also display sorption activity. Novel natural polymer cellulose/chitosan blend beads have been obtained via homogeneous dissolution of chitosan and cellulose in NMMO (Two et al., 2003). Chitosan microspheres with particle size below 3 μm, prepared after a spray-drying process, dissolved readily in NMMO. The cellulose/chitosan blend beads show a rough and folded surface morphology and an interior pore structure. Tests of their deodorizing property against trim ethylamine and of their metal ion sorption properties for $Cu^{2+}$, $Fe^{3+}$, and $Ni^{2+}$ ions indicate that the cellulose/chitosan blend beads have potential applications for odor treatment as well as metal ion adsorption.

An important phenomenon relevant to sorption applications is the solute transport in the membranes or beads; however, the transport behavior of these biomaterial products remains unknown. For large-scale application a deep understanding of the parameters governing solute diffusion within these products is needed. A series of biodegradable cellulose/chitin blend membranes have been successfully prepared from blend solution of cellulose and chitin in 9.5 wt% NaOH–4.5 wt% thiourea aqueous solution by coagulating with 5.0 wt% $(NH_4)_2SO_4$ (Liang et al., 2007). Using a double-cell method and a solution depletion method, the permeability and partition coefficients of three model drugs (ceftazidine, cefazolin sodium, and thiourea) were determined in phosphate buffer solution to clarify the diffusion mechanism governing transport of solutes in these membranes. The membranes exhibited high permeability to the model drugs. The diffusion coefficients of the model drugs increase with increasing temperature and decrease in the size of drug molecule. The permeability of the membranes might improved by increasing the chitin content because of its great contribution to the water-filled pore volume. The transport of drugs through the membranes is primarily by a pore mechanism. The partition mechanism and hindrance effects have also been shown to contribute. Thus, the diffusion of drugs through these membranes occurs by a dual transport mechanism (pore mechanism and partition mechanism) with some hindrance of molecular diffusion via polymer obstruction. The changes of diffusion coefficients and permeability coefficients of the model drugs in the membranes are attributed to the overall effects of these mechanisms.

## 6.3.2  Cellulose/Alginate Blends

Alginic acid is a heteropolysaccharide containing mannuronic acid and guluronic acid groups, and is commonly found in seaweeds (Muzzarelli, 1973). Alginate has been widely used in the fields of controlled release, ion exchange, and the vapor-permeation membrane-separation technique (Chandra and Rustgi, 1998). Alginate membranes show outstanding performance for the dehydration of ethanol–water

mixtures (Yeom et al., 1996; Huang et al., 1999). Moreover, their performance exceeds that of poly(vinyl alcohol) (PVA) and some other polysaccharides with similar chemical structure such as chitosan and cellulose (Uragami and Takigawa, 1990; Shi et al., 1996). The excellent pervaporation performance of alginate membrane is attributed mainly its the extraordinary permselectivity to water in the sorption step (Yeom and Lee, 1998). However, hydrophilicity of the membrane material is not essential for the dehydration process as it can result in a low selectivity and poor strength in aqueous solution at the cost of high flux. Thus, polymer blending techniques should be useful for the preparation of new alginate membranes.

The miscibility and interactions of cellulose/alginate have been studied in cadoxen using the technique of dilute solution viscosity, and a modified treatment basing on Chee's method (Chee, 1990) has been used to determine the miscibility between a stiff polymer (cellulose) and another stiff polymer (alginate) (Zhang L et al., 1998). When the weight ratio of cellulose to alginate is $1:0.1$, the blend is completely miscible and the interaction between molecules of cellulose and alginate is significantly enhanced; when the ratio of cellulose to alginate is lower than $1:0.75$, the blend is immiscible. The strong interactions between the molecules of cellulose and alginate reduce the dominant contribution of the molecular extension of alginate to the viscosity. Blend membranes prepared from regenerated cellulose and sodium alginate in 6 wt% NaOH−4 wt% urea aqueous solution, pre-cooled to low temperature, by coagulating with 5 wt% $CaCl_2$ aqueous solution are miscible at all weight ratios of cellulose to alginate because of strong intermolecular hydrogen bonds between the two polymers and the formation of a $Ca^{2+}$ bridge (Zhou and Zhang, 2001). The membrane surface exhibits a homogeneous mesh structure, and the mesh size increases from 200 to 2000 nm with an increase of alginate from 0 to 80 wt% in the blend membranes, as shown in Fig. 6-4. The mesh structure in the blend membranes is woven from both alginate and cellulose molecules. The crystalline state of the alginic acid membrane prepared from 6 wt% NaOH−4 wt% urea aqueous solution is broken completely, and the crystallinity of the blend membranes decrease with increase of alginic acid. The mechanical properties and thermal stability of the blend membranes are markedly improved compared with the alginate membrane. They thus show promis as separate and functional materials used in the wet state.

Many applications of the ion exchange equilibrium principle have been considered to solve two important environmental problems: the recovery and enrichment of valuable ions, and the removal of undesirable ions from waste water (Huang and Wang, 1993), especially to extract toxic metal ions (Kedem and Bromberg, 1993). Based on the good miscibility and mechanical properties, cellulose and alginate have been utilized as raw materials to make ion exchange membranes (Zhang L et al., 1997, 1999). Ion exchange membranes have been prepared by coagulating a blend of 6.4 wt% cellulose cuoxam (I) and 3 wt% aqueous alginate solution (II) with a weight ratio of $I/II > 1:1.4$ (Zhang L et al., 1997). The tensile strength of both the dry and wet blend membranes is clearly higher than that of membranes made of pure alginate. The ion exchange capacity is 1.25 meq/g dry membrane for the blend membrane with $I/II = 1:1.4$ by weight, and the ion exchange membrane has excellent reproducibility. In addition, the blends exhibit a moderate miscibility, and the
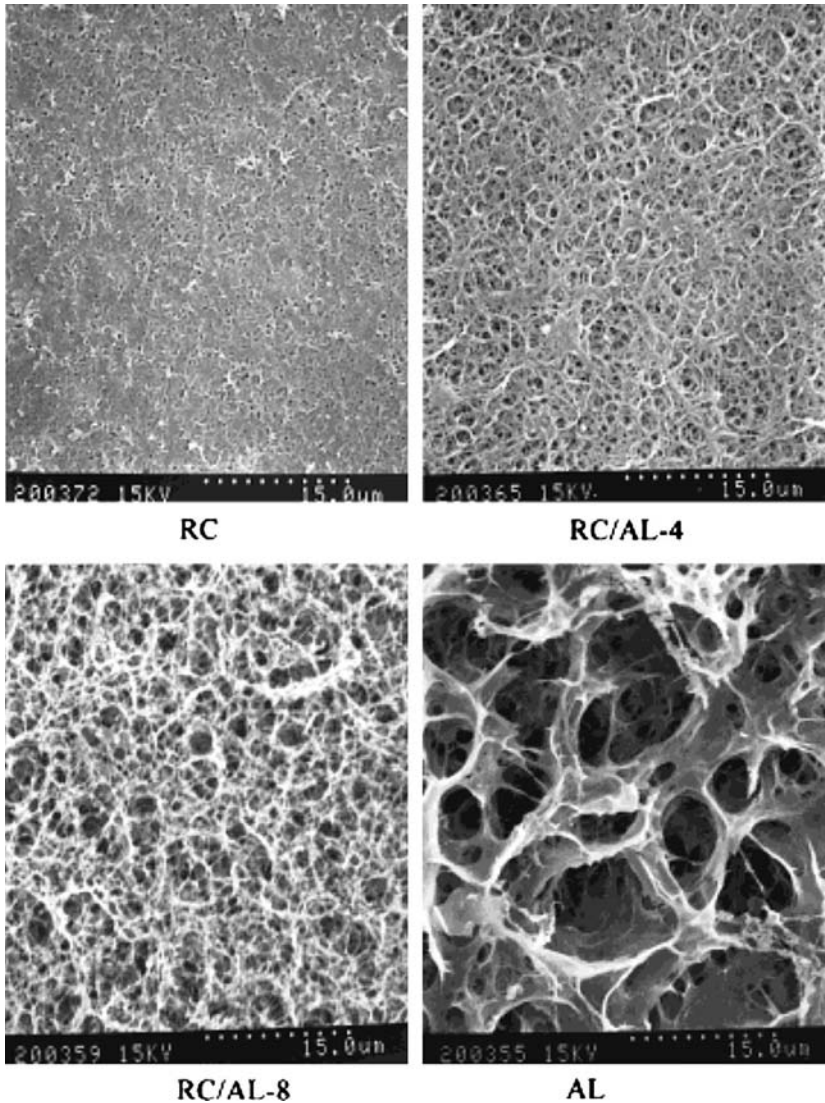
**Fig. 6-4** SEM images of cellulose/alginate membrane surfaces with different sodium alginate contents: RC (0 wt%). RC/AL-4 (40 wt%), RC/AL-8 (80 wt%) and AL (100 wt%). (Zhou and Zhang, 2001).

strong interaction between the cellulose and alginic acid is due to intermolecular hydrogen bonding. The mechanical properties of alginic acid membranes in water are significantly improved by blending with cellulose cuoxam; thus the blend membranes can be used as ion exchange membranes in the water-swollen state.

The adsorption abilities of cellulose/alginic acid ion-exchange membranes have been investigated (Zhang L et al., 1999). The adsorbed amounts ($c_A$) of $Cd^{2+}$ and

$Sr^{2+}$ are 0.79 meq/g at pH 5.8 and 0.75 meq/g at pH 6.0. However, the $c_A$ value of $Sr^{2+}$ for competitive adsorption on the membrane is larger than that of $Cd^{2+}$. The $c_A$ values of $Cd^{2+}$ or $Sr^{2+}$ for single adsorption on the membrane decrease with increasing ionic strength. When EDTA or oxalic acid was added to solutions containing $Cd^{2+}$, $Sr^{2+}$, $Cu^{2+}$, and $Fe^{3+}$, the $c_A$ values of $Cd^{2+}$ and $Sr^{2+}$ for competitive adsorption on the membrane were much larger than those of $Cu^{2+}$ and $Fe^{3+}$, which were captured by the complexing agents to form stable complexes. EDTA enhances the $c_A$ values of $Cd^{2+}$ and $Sr^{2+}$ on the membrane than the others, and the selectivity of metal ions on the membrane is in the order $Sr^{2+} > Cd^{2+} > Fe^{3+} > Cu^{2+}$ in this case. The ion exchange equilibrium was established within 30 min for $Cd^{2+}$ and 90 min for $Sr^{2+}$. The ions adsorbed on the RC-AC membrane are released in 2 mol/l HCl aqueous solution within 10 min.

Pervaporation is a process for the separation of organic mixtures with an azeotropic point, those with similar physical and chemical properties, and aqueous–organic mixtures. It is therefore especially useful for the dehydration of aqueous alcohol mixtures because of the energy-saving efficiency of pervaporation compared with conventional azeotropic distillation (Huang, 1991). Cellulose and cellophane prepared from xanthate cellulose (viscose method) have higher permeation flux in pervaporation of ethanol–water mixtures, but wide application is limited by lack of a good separation factor. Thus, 8 wt% cellulose cuoxam and 8 wt% aqueous sodium alginate solution have been mixed and crosslinked using a $Ca^{2+}$ bridge in 5 wt% $CaCl_2$ aqueous solution to prepare new membranes. The pervaporation separation parameter of ethanol–water mixtures through these blend membranes can be measured with a pervaporation apparatus. For the $Ca^{2+}$ crosslinked blend membranes, which have relatively higher density and crystallinity, the permeation flux hardly changed with decrease of the pore size measured by the flow rate method. Moreover, cellulose/alginate (8 : 2, by weight) blend membranes crosslinked with $Ca^{2+}$ showed higher pervaporation separation factor for 90% alcohol feed mixture at 60°C and higher permeation flux at lower temperature than did noncrosslinked membrane, owing to the $Ca^{2+}$ bridge. The mechanical properties of alginate membranes are significantly improved by introducing cellulose and a $Ca^{2+}$ bridge, and their tensile strength is 12 times that of the pure alginate membrane.

The recent recognition of cellulose as a smart material (Kim et al., 2006a, b) has opened the way for cellulose to be used in biomimetic sensor/actuator devices and microelectromechanical systems. This smart cellulose is termed Electro-Active Paper (EAPap). Its performance is sensitive to humidity, but an EAPap has been made with cellulose and sodium alginate in an aqueous solution of NaOH/urea, which produces its maximum displacement at a lower humidity level (Kim et al., 2007). The d.c. voltage activation shows that sodium ions in the actuator moved to the negative electrode, which defined the ion migration effect in the actuator. When the EAPap actuators were activated with a.c. voltage, the tip displacement output increased with voltage, sodium alginate content, and humidity level. In terms of durability, the displacement of the EAPap actuators decreased with time. The blocked force of the EAPap actuator increased with sodium alginate content. Since this output performance is achieved at room temperature and at moderate

relative humidity levels, an EAPap actuator that is less sensitive to humidity level might be possible. The actuation principle is a combination of two mechanisms: ion migration and the piezoelectric effect associated with dipolar orientation. This combination has the potential for enhancing the properties of this EAPap as a new smart material with a low actuation voltage and fast response along with the many advantages of cellulose material.

### 6.3.3  Cellulose/Protein Blends

***Cellulose/Silk Fibroin Blends***   Silk fibroin (SF), a fibrous protein consisting of glycine, alanine, and serine as the main amino acid residues, is one of the most extensively studied materials because it has good compatibility with the living body (Tanaka et al., 1998) and exhibits oxygen permeability in the wet state (Freddi et al., 1995). SF fibers and membranes have also been used in a glucose biosensor (Liu et al., 1996) and in contact lenses (Minoura et al., 1990), and other applications. However, SF membranes are very brittle (Yamaura et al., 1985) and their changeability and solubility in alkali solution limit wide application. Blending SF with cellulose is a handy and important way to improve their mechanical properties or provide new function.

The effects of coagulants (Yang et al., 2000) and posttreatment with alkali (Yang et al., 2002b) on the structure and micropore formation of cellulose/SF blend membranes have been investigated. Two kinds of blend membranes of regenerated cellulose and SF have been prepared by coagulating solutions of mixtures of cellulose and SF in cuoxam with acetone–acetic acid (4:1 by vol) and 10% NaOH aqueous solutions, coded as RCF1 and RCF2, respectively. The coagulant plays an important role in the structure and micropore formation of the blend membrane (Yang et al., 2000). On coagulation with acetone–acetic acid, RCF1 is composed of cellulose and SF in the ratio of the solution before coagulation. This was attributed to strong interaction caused by intermolecular hydrogen bonding between cellulose and SF, resulting in good miscibility of the blends. The crystallinities of the blend membranes obtained are decreased, and the SF in RCF1 exhibits mainly β-sheet conformation. However, the intermolecular hydrogen bonds between the cellulose and SF in the RCF2 blends are broken in 10% NaOH aqueous solution, which allows most of the SF content to be removed by extraction. Therefore, the cellulose/SF blends prepared by coagulating with 10% NaOH aqueous solution form microporous membranes that as a result of the selective removal of SF become open porous structures. The pore size and water permeability of the microporous RCF2 membranes are greater than those of the RCF1 blend membranes, and increase sharply with increasing of SF content. Since the pore size distribution can be controlled by the conditions of coagulation, the microporous products have promising potential in separation, chromatographic, and biocompatible materials applications.

Furthermore, the RCF1 blend membranes have been subjected to posttreatment with 10% NaOH aqueous solution (Yang et al., 2002b). Alkalies are good solvents for SF, but strong hydrogen bonding between cellulose and SF inhibits the removal of SF, making RCF1 types alkali resistant. In addition, the crystallinity
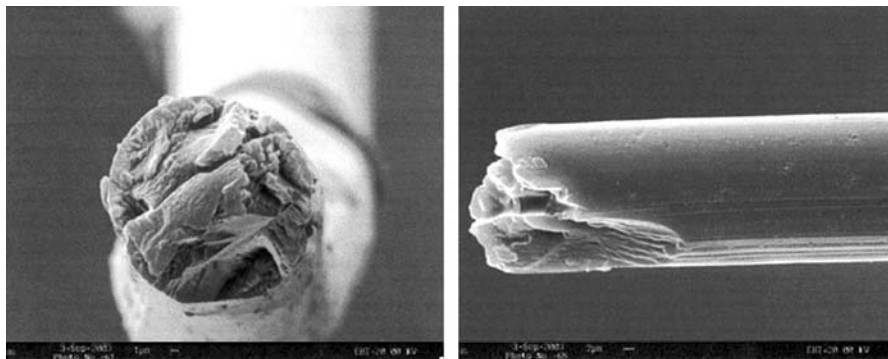
**Fig. 6-5** SEM images of a cellulose/SF blend fiber (Marsano et al., 2007).

and the mean pore size of the blend membranes decrease slightly with increasing posttreatment time, indicating that the cellulose/silk blend membrane can be used under alkaline medium conditions.

Cellulose and silk fibroin are natural, biorenewable, and biodegradable polymers that are widely used in the textile industry. Fibers made of cellulose and SF have been wet spun from solutions in *N,N*-dimethylacetamide containing 7 wt% LiCl, by using different coagulation baths (water and ethanol) and spinning conditions (Marsano et al., 2007). By using water as the coagulant, a partial dissolution of SF can be achieved and there is negligible alteration of the mechanical properties of the cellulose–SF fibers with respect to cellulose fibers. However, fibers coagulated in ethanol are dimensionally homogeneous and have better properties. A modulus of about 13 GPa and elongation to break of 16% for the blend containing 30 wt% SF was obtained with a 20-mm air gap. In particular, X-ray results showed that cellulose–SF fibers are amorphous with a homogeneous dispersion of small SF domains (1.3 nm) in the cellulose matrix. The morphology of a cellulose/SF blend fiber is shown in Fig. 6-5. These results confirmed the good compatibility between the two natural polymers.

***Cellulose/Soy Protein Isolate Blends*** Interestingly, soy protein isolate (SPI) coated onto paper can enhance its grease resistance and mechanical properties (Park et al., 2000), suggesting that an interaction between SPI and cellulose. There is therefore a rationale to blend SPI with cellulose for preparation of novel materials with improved properties and biofunctionality. New blend membranes of cellulose/SPI have been prepared in aqueous solution of 6 wt% NaOH and 5 wt% thiourea by coagulating with 5 wt% $H_2SO_4$ solution (Chen and Zhang, 2004). SPI and cellulose are miscible when the SPI content is less than 40 wt%, and the blend membranes exhibit a mesh structure woven of cellulose and protein chains. The pore structure and properties of the blend membranes are significantly improved by incorporation of SPI into cellulose. With an increase in $W_{SPI}$ from 10 to 50 wt%, the apparent size of the pore ($2r_e$) measured by SEM for the blend membranes increases from 115 nm

to 2.43 μm, and the pore size ($2r_f$) measured by the flow rate method increases from 43 to 59 nm. The tensile strength ($\sigma_b$) and thermal stability of blend membranes with lower than 40 wt% $W_{SPI}$ are higher than those of the pure cellulose membrane, as a result of the strong hydrogen bonding between hydroxyl groups of cellulose and amido groups of SPI molecules. The values of tensile strength and elongation at break for the blend membranes with 10 wt% $W_{SPI}$ reach 136 MPa and 12%, respectively. It is notable that blend membranes containing protein can be used in water because their $\sigma_b$ values in the wet state remain in the range 10–37 MPa. These blend membranes (CS1) can be hydrolyzed with 5 wt% NaOH aqueous solution to obtain membranes designated CS2 (Chen et al., 2004). The CS2 membranes possess microporous structure as a result of the removal of SPI during the NaOH-hydrolysis process, and their pore size increases with an increase of SPI content. The values of $2r_f$ (47.7–77.2 nm) and UFR (28–53.5 ml h$^{-1}$ m$^{-2}$ mmHg$^{-1}$) of the CS2 microporous membranes are higher than those of the corresponding CS1 membranes and pure cellulose membrane, and the microporous membranes also retained high tensile strength in both dry and wet states. In addition, the CS2 membranes containing a small amount of SPI are suitable for the culture of Vero cells. SEM images of Vero cells cultured on the free surfaces of the membranes are shown in Fig. 6-6. These membranes could be candidates for application in separation technology and biomedical fields.

***Cellulose*/*Casein Blends*** Blend membranes of cellulose/casein were prepared from their cuprammonium hydroxide solution to produce membranes having good permeability and excellent mechanical strength (Zhang LN et al., 1995; Yang et al., 1997). The blends are miscible when the casein content is less than 15 wt%, and the mechanical properties of both the dry and wet blend membranes are superior to those of the pure regenerated cellulose membranes; their mean pore diameters and permeabilities are also improved. Extensive research has been done using circular dichroism (CD) measurements on the mixed solutions of cellulose/casein cuoxam and on their gel membranes obtained by alkali coagulation directly or after vaporization of ammonia to detect the phase-separation by optical anisotropy (Yang et al., 1997). The blend membranes with 10 wt% casein show the longest-wavelength CD peak for the charge transfer excitation of the cellulose/cuprammonium complex, while these gel membranes give the highest tensile strength and crystalline orientation. The CD measurements on the mixed solution and gel membranes reveal that the mixed solution with more than 30 wt% casein formed an independent casein/cuprammonium hydroxide complex, giving optically anisotropic phase-separated states; this upper limit shifts toward lower casein content during coagulation.

## 6.3.4 Cellulose/Konjac Glucomannan Blends

Konjac glucomannan (KGM), a natural polysaccharide is composed of β-1,4-pyranoside bond linked mannose and glucose (Shimahara et al., 1975; Maeda et al., 1980) is
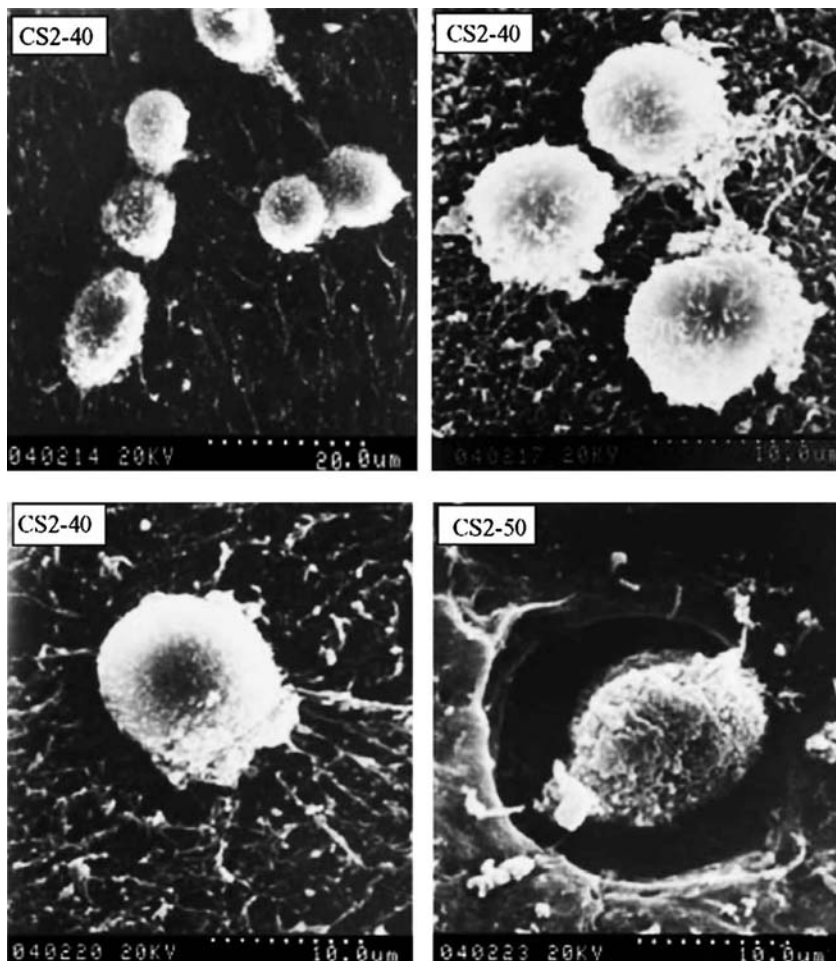
**Fig. 6-6** SEM images of Vero cells cultured on the free surfaces of CS2-40 (40 wt% SPI) and CS2-50 (50 wt% SPI) membranes (Chen et al., 2004).

similar to cellulose. It is known that KGM can be gelled by salts and alkalies, and has potential uses as a thickener and food additive (Nishinari et al., 1992). The crystal structure of KGM has been found to depend strongly on glucose content and temperature. These physical-chemical characteristics and properties of KGM have prompted series of studies on the KGM/cellulose blend system.

Cellulose/KGM blend membranes were first prepared in cuprammonium solution with different coagulations (aqueous 10 wt% NaOH solution or water) at different temperatures (20 or 40 °C) (Yang et al., 1998). The blend membranes are miscible with 0–30 wt% content of KGM, and the tensile strength, pore size, and water

permeability of cellulose/KGM blend membranes can be affected by the coagulating conditions. Similar research on preparing cellulose/KGM blend membranes has used precooled NaOH/thiourea aqueous solutions by coagulating with 5 wt% $CaCl_2$ aqueous solution (Yang et al., 2002a). In this solvent system, cellulose and KGM are miscible over the whole range of their weight ratios. The blend membranes are "alloys" of cellulose and KGM, and form mesh structures woven of two polymers. New crystalline planes form due to the similarity of structures and interaction between cellulose and KGM. With an increase of the KGM content, pore size and water permeability of the blend membranes rapidly increase, then reach a plateau at about 50 nm at $w_{KGM} \geq 30\%$. The tensile strength and breaking elongation of the blend membranes in the dry state decrease slightly and then decrease significantly at $w_{KGM} \geq 50\%$. The content of through-pores of the cellulose membranes blended with KGM increases, and the pore size distribution becomes wider, compared with pure cellulose membrane. KGM plays an important role in the formation of through-pores in the microporous membranes, leading to higher water permeability. This is thus a novel way to prepare membranes and porous gel particles with various pore sizes for application in the field of separation.

Size-exclusion chromatography (SEC) is an important technique in the analysis and quality control of polymers (Churms, 1996; Lundahl et al., 1999). The chromatographic packing materials for separation of biopolymer are mostly prepared from polysaccharides (Gustavsson and Larsson, 1996; Noel et al., 1996) or inorganic packings coated with polysaccharides (Petro and Berek, 1993, 1994; Castells and Carr, 2000; Chen et al., 2002). Cellulose has great potential for use as a chromatographic packing because of its characteristics of good solvent resistance, biocompatibility, biodegradability, and relatively low cost. Recently, novel microporous beads of particle size about 90 μm have been prepared, for the first time, from cellulose and konjac glucomannan (RC/KGM) in 1.5 M NaOH−0.65 M thiourea aqueous solution by an emulsification method (Xiong et al., 2005). The microporous beads were then modified with silane to avoid the adsorption of polymers containing hydroxyl groups; these are coded as RC/KGM-Si. The morphology of these beads with and without modification is shown in Fig. 6-7. A preparative SEC column (500 mm × 20 mm) is packed with RC/KGM-Si; its exclusion limit and fractionation range of the stationary phase are, respectively, weight-average molecular mass ($M_w$) of $4.8 \times 10^5$ g/mol and $5.3 \times 10^3 - 4.8 \times 10^5$ g/mol for polystyrene in tetrahydrofuran. A preparative SEC column has been used to fractionate poly(ε-caprolactone) (PCL; $M_w = 8.31 \times 10^4$ g/mol, polydispersity index $d = 1.55$) in tetrahydrofuran and a polysaccharide (PC3-2; $M_w = 1.21 \times 10^5$ g/mol, $d = 1.70$) in 0.05 M NaOH aqueous solution. The $M_w$ values of the fractions determined by analytical SEC combined with laser light scattering range from $1.2 \times 10^4$ to $1.84 \times 10^5$ for PCL and from $8.5 \times 10^4$ to $2.13 \times 10^5$ for PC3-2; $d$ values are in the range 1.2−1.5. Preparative SEC has good fractionation efficiency in both organic solvents and alkaline aqueous solutions for the various polymers, leading to the promise of application in polymer separation.
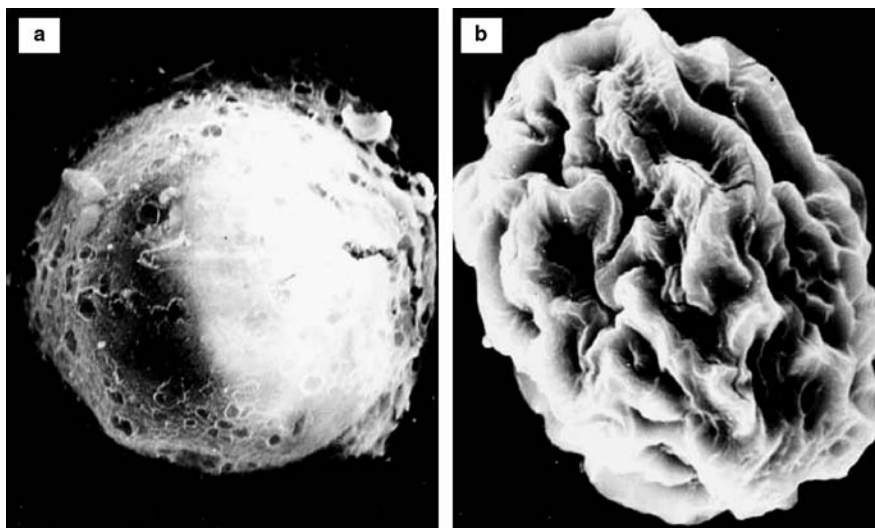
**Fig. 6-7**    SEM images of RC/KGM (a) and RC/KGM-Si (b) (Xiong et al., 2005).

## 6.4    CELLULOSE DERIVATIVE/NATURAL POLYMER BLENDS

Cellulose esters of inorganic and organic acids, as well as cellulose ethers, are pioneer compounds of cellulose chemistry and remain the most important technical derivatives of cellulose. In recent years, various cellulose derivatives (esters or ethers) mixed with natural polymers have been studied and developed in order to obtain new blend materials with multiple applications.

### 6.4.1    Blends Containing Cellulose Ethers

The synthesis of cellulose ethers is an important aspect of commercial cellulose derivatization. Cellulose ethers have outstanding properties, good solubility, and high chemical stability, and are toxicologically innocuous. The especially important parameter of water solubility can be controlled to a certain extent by the constitution and combination of the ether groups, the degree of substitution, and the distribution of substituents. Cellulose ethers, such as hydroxyethyl cellulose (HEC), methyl cellulose (MC), ethyl cellulose (EC), hydroxypropylmethyl cellulose (HPMC), and carboxymethyl cellulose (CMC), can be also blended with various natural polymers to obtain new composite materials with multiple applications.

The miscibility of blends of chitosan and a series of cellulose ethers—HEC (Wali et al., 2005), MC (Yin et al., 2006), and HPMC (Jayaraju et al., 2006; Yin et al., 2006)—in acetic acid solution has been studied. Blends of chitosan/HEC are completely miscible in all proportions. However, blends of chitosan/MC are not fully miscible in the dry state, and those of chitosan/HPMC are miscible when the chitosan

content is >50%, although weak hydrogen bonding exists between the polymer functional groups.

HEC, a nonionic water-soluble and water-swellable cellulose ether, is compatible with a wide range of other water-soluble polymers (Adeyeye and Price, 1991; Dalal and Narurkar, 1991; Downs et al., 1992). It is a commercially useful polymer that finds applications as a thickener in latex paints and paper finishes. Pervaporation separation membranes of sodium alginate and HEC have been prepared by solution casting, crosslinked with glutaraldehyde and urea/formaldehyde/sulfuric acid mixtures (Vijaya et al., 2005a, b). Membranes were tested for pervaporation separation of feed mixtures ranging from 10–50 wt% water in water/1,4-dioxane and water/tetrahydrofuran mixtures at 30°C. For 10 wt% of the feed mixture, pervaporation experiments were also done at higher temperatures (40 and 50°C). On increasing the temperature, a slight increase in flux with a considerable decrease in selectivity is observed for all the membranes and for both the mixtures. The blend membranes exhibit different pervaporation performance for both the binary mixtures investigated. For water/1,4-dioxane mixture the pervaporation performance did not improve much after blending, whereas for water/tetrahydrofuran mixture the pervaporation performance was improved considerably over that of plain sodium alginate membrane. Similarly, blend membranes of sodium alginate and HEC have been synthesized and ionically crosslinked with phosphoric acid for the separation of $t$-butanol/water mixtures (Kalyani et al., 2006). The crosslinked polymers have good potential for breaking the azeotrope of 88 wt% $t$-butanol by giving high selectivity of 3237 and substantial water flux of 0.2 kg m$^{-2}$ h$^{-1}$. The pervaporation performance is evaluated by varying experimental parameters such as feed composition, membrane thickness, and permeating pressure, and is promising for $t$-butanol dehydration.

A variety of polymers have been used for developing controlled-release formulations to enhance the release rates of drugs. Among various polymers employed, hydrophilic biopolymers are suitable in oral applications because of their inherent advantages over synthetic polymers. Controlled release of diclofenac sodium (DS) and ibuprofen (IB) drugs through sodium alginate–HEC blend polymeric beads was investigated (Krishna et al., 2006). Beads are prepared by precipitating the viscous solution of sodium alginate/HEC blend in alcohol followed by crosslinking with calcium chloride. The beads formed are smooth with nonporous surfaces, as seen in the SEM image shown in Fig. 6-8. The DS-loaded beads show better release performance than the IB-loaded beads. Diffusion parameters have been evaluated from Fick diffusion theory. Mathematical modeling studies and drug release characteristics through bead matrices involve solving Fick's diffusion equation. Carbohydrate polymeric blend microspheres with controlled release properties, consisting of sodium alginate and MC have been prepared by a water-in-oil (W/O) emulsion method (Ramesh et al., 2007). These microspheres are cross-linked with glutaraldehyde and loaded with nifedipine (NFD), an anti-inflammatory drug. The drug can be released in a controlled manner. Swelling studies of microspheres show that water uptake decreases with an increasing amount of MC in the microspheres. This effect is correlated with the release rates of the drug though the microspheres containing different amounts of MC. The microspheres have lower
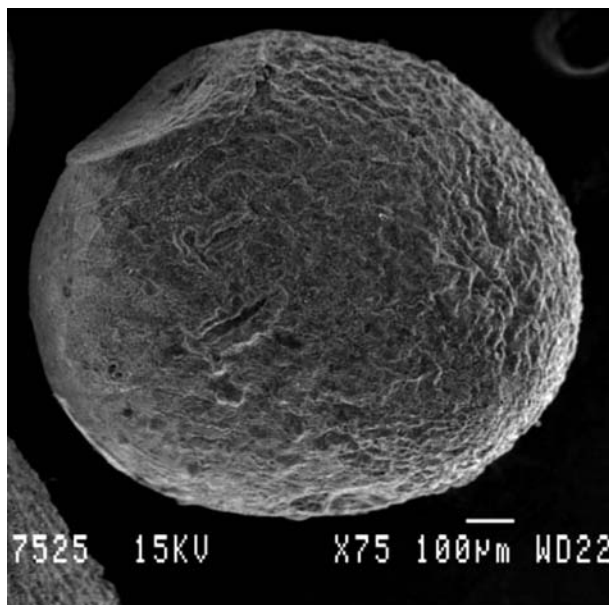
**Fig. 6-8**    SEM image of a sodium alginate/HEC bead (Krishna et al., 2006).

densities and hence should be retained in the gastric environment for more than 12 hours, which would help to improve the bioavailability of nifedipine.

Chitosan can also be blended with a hydrophobic coating material, in ratios appropriate to provide desirable drug release rates from core tables or pellets. Thus, EC can be chosen as the major coating component and chitosan as the minor component to form blended coating films determine the most promising proportion range for practical application (He et al., 2006). Dry films have been produced by a casting/solvent evaporation method, with different volume ratios of EC and chitosan solution and various plasticizers. Wet films can be prepared by immersing dry films in pH 6.8 phosphate-buffered saline (PBS) for 24 hours. Promising ratios of EC to chitosan are below 20 : 5 or 20 : 6 with various plasticizers, determined by comparing the viscosity of the blended solutions and the morphology of the blended films. All the plasticizers tested have good compatibility with EC or chitosan; dibutyl phthalate (DBP) has the greatest efficacy, inducing the lowest $T_g$ (39.9°C) of the film. The release rates of tetramethylpyrazine phosphate (TMPP) from pellets coated with the blended films of EC/chitosan (20 : 6 v/v) with various plasticizers show that the more water-soluble the plasticizer is, the more quickly is TMPP dissolved from the coated pellets. This further indicates that the water-insoluble plasticizers (such as DBP) could be more suitable for producing the sustained-release or controlled-release property of the blended films in wet state.

CMC, a cellulose derivative formed by the carboxymethylation of the hydroxyl group in cellulose, can act as an ion-exchange material for carboxyl groups (Lali et al., 2000; Aruna and Lali, 2001). The adsorption of lysozyme has been investigated

with novel macroporous chitosan/CMC blend membranes, which can be prepared by a simple solution-blending method with glutaraldehyde as a crosslinking agent for chitosan and with silica particles as porogens (Chen et al., 2005). The maximum adsorption capacity of the macroporous chitosan/CMC blend membranes is as high as 240 mg/g (170 mg/ml), and more than 95% of the adsorbed lysozyme is desorbed in a pH buffer at 11.8, indicating that the chitosan/CMC blend membranes could act as cation-exchange membranes. In addition, the lysozyme adsorption capacity of the blend membranes increased with an increase in the initial lysozyme concentration and the adsorption temperature. The blend membranes also have good reusability after several adsorption–desorption cycles.

At the same time, interpenetrating network polymeric beads of sodium alginate blended with sodium carboxymethyl cellulose had been prepared by crosslinking with a common crosslinking agent, glutaraldehyde, for the release of the insecticide carbaryl (Işiklan, 2006). It was observed that the carbaryl release decreased with increase in crosslinking of the network, while it increased with increase in carboxymethyl cellulose content in the blend beads and with temperature. Diffusion coefficients were calculated for the transport of insecticide through the polymeric beads, using the initial-time approximation method. These values are consistent with the carbaryl release data, which followed the Fick trend.

### 6.4.2  Blends Containing Cellulose Esters

Among industrially established cellulosic products, organic ester derivatives of cellulose form a valuable family, finding general acceptance in various fields of application such as packaging, coating, release-controllable excipients, molded plastics, optical films, fibers, membranes, and other separation media (Edgar et al., 2001). It is a further attraction that polymer blending may offer opportunities not only to improve the processability and modify the physical properties of cellulose esters, but also to alter the thermal instability and mechanical brittleness of the second component polymers.

It has long been known that cellulose acetate (CA) has good mechanical strength in fabricating hollow fibers. Thus, novel chitosan/CA blend hollow fibers have been prepared by the wet spinning method, in which CA acted as a matrix polymer and chitosan as a functional polymer to provide the product with coupling or reactive sites for affinity-based separations (Liu and Bai, 2005). Formic acid can be used as the cosolvent for both CA and chitosan to prepare the dope solution and NaOH solution is used as the external and internal coagulant in the wet spinning fabrication process. The hollow blend fibers display good tensile stress, though tensile stress reduces with the increase of the chitosan content in the blend. Furthermore, highly porous chitosan/CA adsorptive hollow fiber membranes have been prepared, which exhibit the ability to remove copper ions from aqueous solutions (Liu and Bai, 2006b).

The effects of polymer concentrations and coagulant compositions on the structures and morphologies of blend membranes (Liu and Bai, 2006a) have been investigated (see Fig. 6-9). For CA concentrations of 12–18 wt% and chitosan
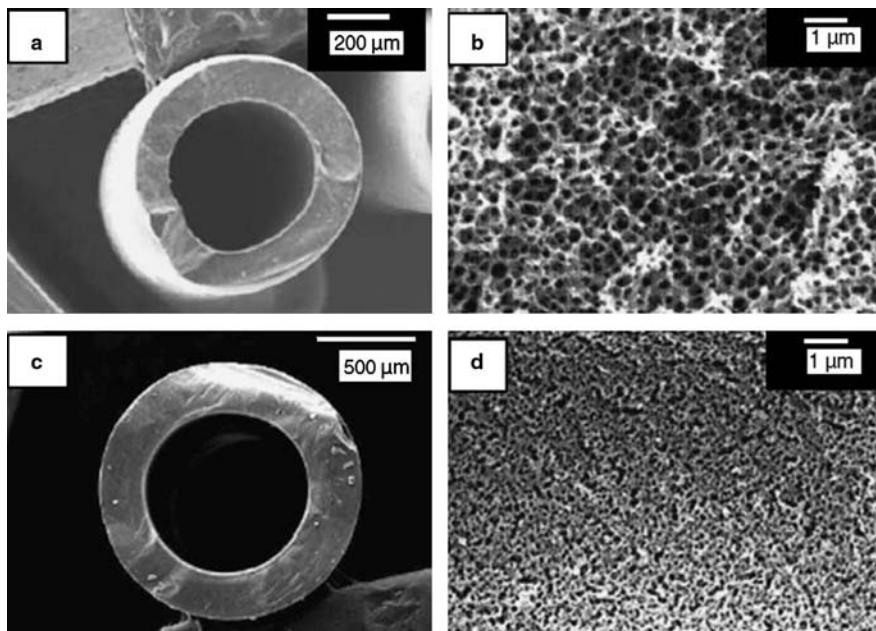
**Fig. 6-9**    SEM images showing the overall (a and c) and cross-sectional (b and d) structures of chitosan/cellulose acetate blend hollow fibers prepared from spinning solutions containing 12 wt% cellulose acetate and 2 wt% chitosan (a and b) and 18 wt% cellulose acetate and 2 wt% chitosan (c and d) (water was used as both the external and internal coagulant (Liu and Bai, 2006a).

concentration up to 4 wt% in the spinning dope solutions, hollow blend fibers have successfully been prepared with outer surface pore sizes, specific surface areas, and porosities in the range of $0.54-0.049 \,\mu m$, $10.4-14.5 \, m^2/g$ and $80.6-70.4\%$, respectively, depending on the amounts of CA and chitosan in the spinning dope solutions and the coagulants used. Water, a weaker coagulant, can be used as both the external and internal coagulant in the fabrication process. The resultant chitosan/CA blend hollow fibers show spongelike, macrovoid-free and, relatively uniform porous structures, which are desirable for adsorptive membranes. With increasing alkalinity of the coagulants, the coagulation rate of the hollow blend fibers increases and the fibers can be observed to form relatively denser surface layers and to have smaller surface pore sizes and slightly greater specific surface areas, due to the stronger coagulation effect. In particular, when NaOH solutions $(1-3 \, wt\%)$ were used as the internal coagulant, more and larger macrovoids were formed in the hollow fibers at the near-lumen side with increase of the NaOH concentration at low chitosan concentrations $(<3 \, wt\%)$. In addition, chitosan/CA blend hollow fiber membranes have good adsorption capacity (up to $35.3-48.2 \, mg/g$), fast adsorption rates, and short adsorption equilibrium times (less than $20-70 \, min$) for copper ions. Moreover, they can work effectively at low copper ion concentrations $(<6.5 \, mg/l)$

to reduce the residual level to as low as 0.1–0.6 mg/l in the solution. The adsorption of copper ions on chitosan/CA blend hollow fiber membranes is attributed mainly to the formation of surface complexes with the nitrogen atoms of chitosan in the hollow fiber membranes; hence higher chitosan contents in the hollow blend fiber membranes render the membranes more adsorptive to copper ions. It has been found that the copper ions adsorbed on the hollow fiber membranes can be effectively desorbed in an EDTA solution (up to 99% desorption efficiency) and the membranes can be reused almost without loss of adsorption capacity for copper ions.

## 6.5 PROMISING APPLICATIONS OF CELLULOSE BLENDS

Cellulose is playing an increasingly important role in the development and application of natural polymer materials, and has attracted a great deal of attention. Because of the abound OH groups and good compatibilities, cellulose and its derivatives can be blended more easily with other natural polymers to obtain novel biodegradable materials with unique functions and good properties. These blends can be expected to substitute for a proportion of synthetic polymers. In the meantime, the development of solvent systems for cellulose, especially the invention of new
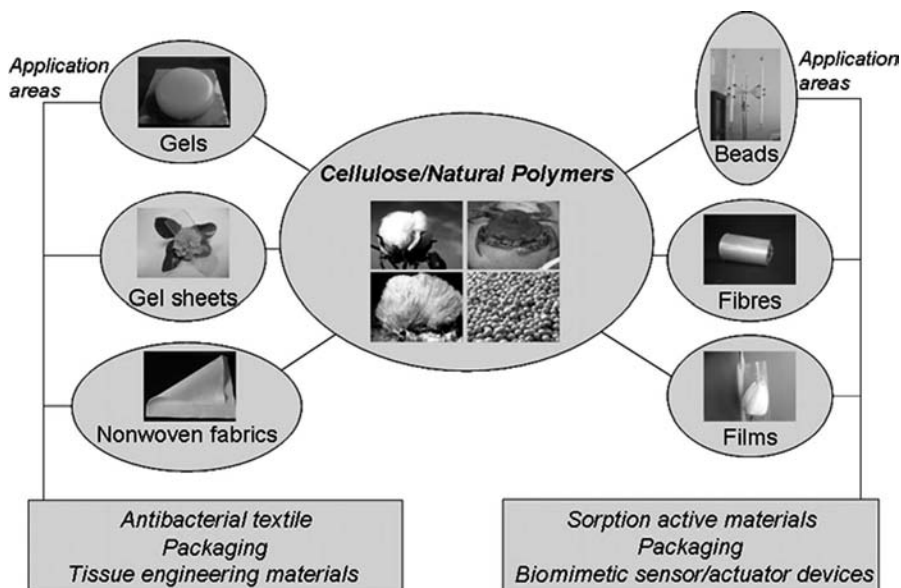


**Scheme 6-1** Products and applications of cellulose and cellulose/natural polymer blends. The photographs show cellulosic beads, fibers, films, gels, and gel sheets prepared from cellulose solution in NaOH/urea or NaOH/thiourea solvent systems via "green" processes; the nonwoven fabrics are commercial products.

nonpolluting solvent systems, provides a "green" path for preparation of composites based on cellulose, and makes it possible to implement industrial production.

Scheme 6-1 shows potential applications of cellulose and cellulose/natural polymer blends. The cellulosic beads, fibers, films, gels, and gel sheets illustrated have been successfully prepared from our cellulose solution in NaOH/urea or NaOH/thiourea solvent systems by "green" processes; the nonwoven fabrics shown are commercial products. These cellulosic blends exhibit not only the native properties of the components but also a significant synergistic effect caused by the interactions between cellulose and other natural polymers. As mentioned above, cellulosic composites containing chitin/chitosan exhibit good bactericidal properties, and accordingly the corresponding fibers and cloth can be used to produce antibacterial textiles. Many of the cellulose/natural polymer blends form microporous structures and can be used for sorption active materials that are biosorbent for the removal of heavy metals, packings for size exclusion chromatography, and the controlled release of drugs. Cellulose/natural polymer blends also possess good biocompatibilities and thus can produce materials for packaging and tissue engineering. Recent discoveries provide a way for cellulose to be used in biomimetic sensor/actuator devices and microelectromechanical systems. This opens a new field for the application of cellulosic materials that can be expected to show further improvement in the future. Nowadays, the goal of the creation of a biobased economy is a challenge to agriculture, forestry, chemistry, and industry. Natural polymers from plants are renewable resources, and their products can be biodegraded in the soil or in lakes at the end of their use life. These new products blending cellulose and natural polymers meet present requirements concerning environmental protection and sustainable development.

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